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METALS & ALLOYS

Volume VIII—January, 1937 to December, 1937

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What Hasn't Been Accomplished in 1936

by H. W. Gillett

THE JANUARY ISSUES of many technical journals carry surveys of the accomplishments of the previous year. With the re-inauguration this month of the leader of the Squanderbund and the prospects of what may happen in the next four years, one wonders whether it makes a heck of a lot of difference whether or not progress has been made or will be made toward solution of the technical problems attending the production of better and cheaper things that satisfy human desires, raise the standard of living and provide employment. Personally, we class as a thoroughly unreconstructed rebel who still believes in the precepts of Ben Franklin rather than those of Franklin D. Some 17 million voters of the same mind form a minority, it is true, but not so small a one that we feel too lonely.

We are consoled by the thought that the proportion against our point of view is, after all, only one and a fraction to one. Even a large numerical majority doesn't necessarily mean that the majority is right. Consider the apparent solidarity of the German people behind Hitler. Does the huge majority he is able temporarily to command mean that it is really right, or even profitable in the long run, to shoot your political opponents? What those who happen to have been put in positions of power by mass hysteria need most is the continued frank opposition of those who disagree with their aims, principles, or methods. Hence, we view with alarm the after-election editorials of part of the business and technical press to the effect that, whatever we really think, we should go along with the administration and keep our mouths shut. That was done four years ago when, in the first flush of the administration, everyone was hopeful that a Moses had appeared to lead us out of the wilderness, and it was that going along that led to the imposition upon us of N.R.A. and other unworkable schemes.

An analogous point of view might be brought to bear on this matter of recent progress. Certainly there has been technical progress, but are we justified only in pointing with pride, and refraining entirely from viewing with alarm?

Back in 1894, Thomas Blair reported that "1 per cent molybdenum rendered good iron red-short and utterly worthless." That "information" could have been cited in the January, 1895, journals among the "useful facts" brought out in the previous year, had such reviews then been in vogue. So we might ask how far we really broke away in '36 from repeating as fundamental truths, things that never were true in the first place.

The "Nuisance" Elements

In respect to the alleged evil effects of Cu and P in steel, some wiping out of misapprehensions has occurred, and we know more as to the conditions under which the old ideas are true and those where they are false. But we still know very little about the mechanism that produces phosphorus embrittlement when it does occur. How many other "nuisance" elements or merely neglected elements are waiting around for someone to find out where they can really be of service? K.C.Li., in Mathewson's "Modern Uses of Nonferrous Metals," remarked that much arsenious oxide has been bonded with cement, taken out to sea and dumped, just to get rid of it. Well-rounded progress ought to have pointed the way for use of arsenic. In the list of less common elements, uranium is still waiting around, while columbium has become of vital importance in its one application in 18:8.

Some progress has been made in wiping out the theory of undissolved graphite nuclei in the melt as the one thing to be avoided in the production of high test cast iron, and alternate theories have been promulgated. Releasing our minds from that groove is a help, but the new grooves don't seem to be leading any place in particular, and the real facts as to superheating and the like are by no means clear as yet. We're not justified in being too complacent about our understanding of cast iron.

The Open-Hearth and Blast Furnace

The past decade has seen advances in open-hearth practice along lines of thermal economy and in the

application of physical chemistry. Blast furnace operation could do with analogous study. Would it not be better to purify the charge from much of the silica it ordinarily carries, ship less weight and carry less slag? Do we really need slag volume and fuel to melt it? Cupola, electric, air furnace and various other melting methods should be benefited by the method of attack used on the open-hearth problem, and the last word is far from said on that. How about a really acceptable method for measuring the temperature of molten steel in any sort of furnace?

Despite all the work on machinability and free-machining steels, we are a long way from having untangled the variables or having developed a real test to evaluate the property.

Grain size control in steel is becoming more truly under control, but we still grope for complete and adequate explanations. Controlled atmospheres for heat-treating advance commercially, but largely by cut and try methods, with a fool-proof, simply produced, and universally applicable atmosphere still to be found. In this connection, wouldn't it be nice if some one would show how to handle steel in soaking pits, and in rolling and forging, without scaling?

Even the protection of the surface of unalloyed iron and steel from atmospheric corrosion is pretty much where it was ten years ago, but that isn't primarily the metallurgist's problem. His problem, of cheaply producing corrosion resistant alloys or metallic surfaces, has yielded somewhat to attack, but the situation is still far from satisfactory. For example, how much real progress has been made toward getting plated or hot-dipped coatings that are truly free from pinholes and other flaws?

Corrosion, Abrasion and High Temperature

The severe-service applications, where corrosion, abrasion, or high temperatures are involved, are probably those we can design for with the poorest degree of assurance. With all the work on corrosion, in an apparently fairly simple case of the stainless tanks for gasoline and sea-water for its displacement on the Navy vessels, foresight was not so good as hindsight, and the hindsight doesn't seem any too clear at that. With lots of new low-alloy high-yield strength steels and the need to know how they will behave under various corrosive conditions, where is the reliable method for predicting just how they really will behave in the long run?

Observation of wear resistant alloys in actual service involving severe abrasion is under way that may bring out some specific facts, but how unlikely it is that even if the tests lead to definite conclusions, the same alloys will be put through a series of different types of laboratory wear tests to show which, if any, give true indications?

As to high temperature service, we have repeatedly commented on the peculiar situation where supposedly duplicate heats behave widely differently in long-time load carrying ability, with very little done about remedying the situation. And, speaking of temperature, what is the real cause of low impact at low temperatures in a host of alloys?

As to endurance under repeated stress, progress was made by large jumps a few years ago, but a lot of subsidiary problems of engineering importance were raised, whose solution seems to be coming very slowly. Professor Moore, to whose efforts so much of the past progress is due, in characteristic fashion, raised a whole series of questions on endurance to which answers have not yet been forthcoming, at the "Symposium on Plastic Behavior of Metals" last fall.

Bearing Metals

New bearing metals have come on the scene, some of them bringing headaches to the oil men, others alleged to be better on this or that score, but who knows just what quantitatively measurable properties are wanted in a bearing, anyhow? We wish user engineers would give this more thought, just as we wish that structural engineers and the like would define the amount of ductility and the kind of toughness they actually need in an alloy instead of demanding just the elongation they are used to specifying for some quite different alloy.

While we are talking about other engineers than metallurgical engineers, how about having the electrical engineer give us high frequency generators at low enough cost so that we can do more metallurgical stunts with inductive heating, and how about having the ceramic engineer supply refractories that will give a decent life in rotary melting furnaces to be operated on steel, or even on really superheated cast iron?

Gases in Metals

Returning to metallurgical engineering, consider "gases in metals," so commonly discussed. Aren't we saying about the same things we said ten years ago, and in nearly as vague a fashion, without much more clear proof as to truth or falsity of the ideas?

How about metallic resistors for high temperature work that don't have to be babied in one way or another?

Where is the solder to meet the temperature range half way between the soft solders and the silver solders? And for that matter, where are the tarnish-proof silver or copper alloys? Where are the high conductivity, high strength alloys that are cheap and readily cast and fabricated?

A few months ago, we heard one of the best authorities on austenitic alloys discuss 18:8 and its close relatives. His talk was steadily interspersed with points which he listed as needing exhaustive study before facts could be brought out that would remove many phases of the topic from empiricism. And if anybody tried to give a similar talk on the heat-resisting alloys, such comment would be doubly true.

(Continued on page 24)

METALS AND ALLOYS IN THE

Printing Industry—1

by B. W. Gonser and S. Epstein

Battelle Memorial Institute, Columbus, Ohio

THE PRINTING INDUSTRY is the fifth largest industry in the country, the value of its product in 1933 amounting to over $1,500,000,000. It is a large user of metals both as structural material for its plants, printing presses, and other machinery, and as type metals, photoengravings, electrotypes, stereotypes, lithographic and gravure plates, and plate mounting bases. In the rapidly growing art of printing on tin plate, metal foil, and metallized paper, the printing surface is itself metallic. Metal powders are also frequently used in compounding for printing inks and dusting.

The beauty, accuracy, and low cost of modern printing in general, the remarkable beauty and fidelity of multicolor printing in particular, and the speed and fine quality of newspaper and magazine printing would be impossible without metals. Metallurgical developments have aided greatly in attaining this status. Yet the average metallurgist knows very little about the printing industry and the average craftsman in the printing industry knows little about metallurgy. A better acquaintance should be of mutual interest and may help accelerate further advances.

There are three general classes of printing—letterpress, where the printing areas are in relief; planographic, where the printing and non-printing areas are relatively in the same plane; and intaglio, where the printing areas are below the surface. Offset lithography is the most widely used of the planographic processes and gravure of the intaglio processes.

LETTERPRESS PRINTING

LETTERPRESS printing is by far the most commonly used method. About 75 per cent of all the printing in the country, almost all newspaper printing, and the great majority of magazine printing is letterpress. Type-matter is printed from raised letters, these being "composed" mainly by mechanical composing machines of which the linotype and monotype machines are best known. Some type is still set by hand.

Linotype

As the name indicates, the linotype machine casts a single line of type at one time. The operator sits at a keyboard and as he presses a key a lever causes a brass matrix with the letter cut into its edge to be released from a magazine. The matrix is carried automatically to an assembly box, when the line is completed, a lever is depressed which causes the matrices (and proper spacers) to be carried to a position in front of the mold, behind which there is a pot of molten linotype metal. A plunger in the metal pot then forces some of the molten metal against the face of the matrices. The resultant slug with the letters in relief is automatically trimmed for height and thickness prior to its being ejected onto a receiving galley. The matrices or small pieces of brass, varying in thickness with the width of the letter, are meanwhile automatically redistributed in the magazine.

Nearly all newspapers are composed with linotype machines. As in a large portion of letter press printing, however, the large newspapers are not printed directly from the type (linotype). Instead the type is used only as a mold for stereotyping. In this process the type is molded into a paper composition mat, the full size of the newspaper page. This mat, in turn, acts as a mold in a suitable casting box in which molten stereotype metal is cast into a curved plate that may be

Casting Unit of the Monotype Typesetting Machine Delivering Type. (Courtesy Lanston Monotype Machine Co.)

readily attached to the surface of the cylinder of the printing press. The chief advantage of stereotyping is that a number of matrices may be made from the originally composed type and a number of stereotypes may be successfully cast from each mat. A number of presses may consequently print the same edition simultaneously. It also offers the most rapid simple means of making curved plates for rotary printing. Illustrations can be readily incorporated along with the type matter.

Monotype

The monotype process produces properly spaced lines of individual type characters. Two separate machines are used, the keyboard and the caster. As the operator depresses the keys on the keyboard, holes are punched into a strip of paper similar to a player piano roll. When the roll is completed, it is transferred to the casting machine. In this machine the perforations on the paper roll control the mechanism which brings the respective matrices into position as a jet of metal is forced into the mold and the type is cast.

While the monotype machine is not as speedy as the linotype, it is nevertheless very rapid; as many as 250 or more letters can be cast in one minute. Higher quality printing can be done with monotype composition than with linotype. Still finer work can be done with hand set foundry type. For large editions it is not customary to print from the original type and duplicate printing plates are reproduced by the stereotype process or by the electrotyping process which will be described later.

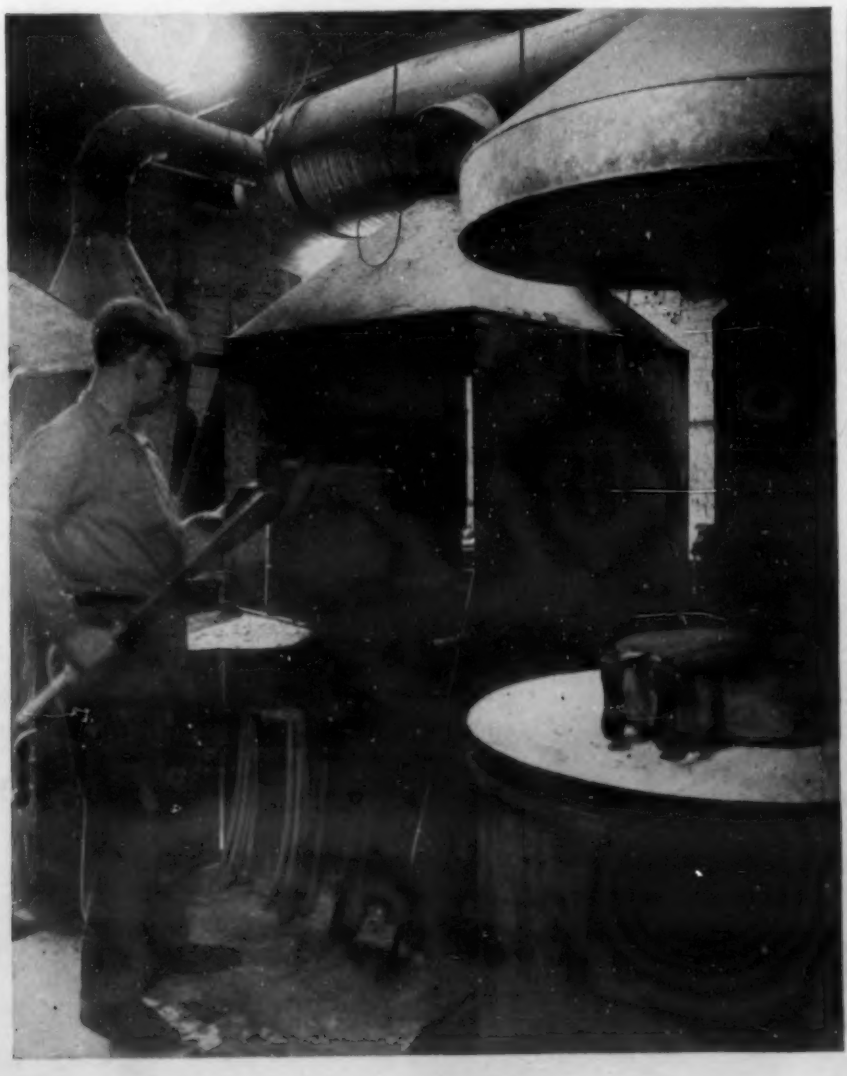
Photoengraving

So far type matter only has been discussed. Coming to letter press illustrations, these can be divided into line etchings and half tones. For line etchings a relief printing surface is obtained, usually on zinc plates about 0.065 in. thick, by photochemically reproducing the pattern on a sensitized emulsion on the plate. In the "cold top" process, for example, the emulsion consists of shellac impregnated with bichromate salts or something similar. Parts exposed to light become insoluble and remain unaffected, while the soluble portions are washed away (i.e. developed) with a suitable solvent. The zinc plate is then etched in about a 10 per cent nitric acid solution so that the non-printing surface of the plate is etched away and the printing surfaces stand out in relief. In line etchings shading is obtained by varying the proximity and width of the lines.

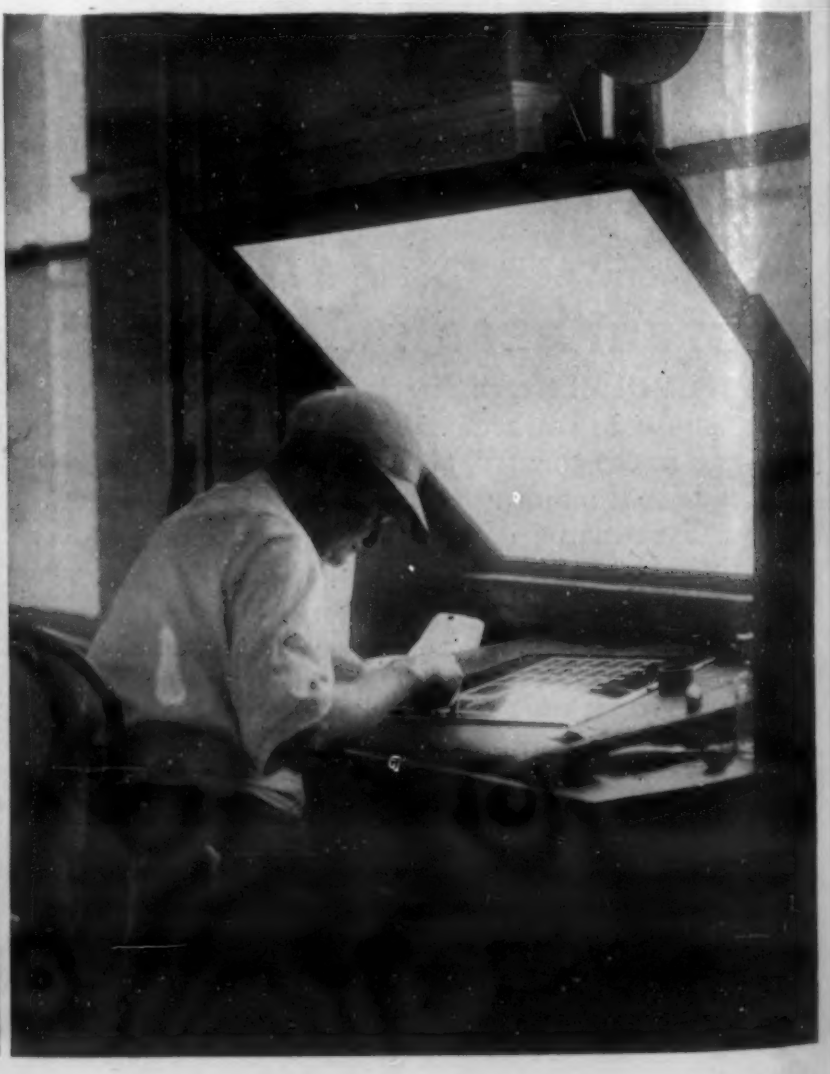
By another method of plate preparation, the "ink top" method, the zinc is coated with a film of bichromated glue and dried. A photographic print is then made on this surface through a negative. The entire surface is then inked with a special ink and the resultant surface developed by wiping off the ink covered soluble portions (unexposed areas) with a wad of cotton under a stream of water. The inked image remaining on the zinc is dusted with a powdered fusible resin (dragon's blood) and heated until the resin fuses, thus forming an "acid resist" over the image.

This is for simple black and white printing. Tonal gradations, such as are present in wash drawings and

Hardening Steel Engraved Plates.
(Courtesy U. S. Bureau of Engraving and Printing)



Finishing Engraved Plates.
(Courtesy U. S. Bureau of Engraving and Printing)



photographs, are reproduced by the half-tone process —an ingenious way of printing the various gradations in tone, from almost pure white to gray and black, with black ink. As is well known, a fine screen is used for breaking up the tones in the original. The image, photographed through the screen, is transferred to the metal plate as for line drawings.

Note: Copper plates instead of zinc plates are used for half-tone engravings (except where coarse screens are desired); a ferric chloride solution is then used for etching.

After etching, the relief printing surfaces, instead of being continuous lines, consist of dots which vary in size from the most minute pin points in the high-lights of the original to larger dots in the middle tones and solid black in the darkest portions of the picture. When the plate is printed, the difference between the blacks and the light tones is due to the open spaces between the dots; the dots stand out in relief and make the printed impression.

The same principle is applied for color work. By properly combining the three primary colors and black, any secondary color may be reproduced. The yellow plate is produced by photographing through a blue filter, the red plate through a green filter, and the blue plate through a red filter. As the negative for each color is made, the half tone screen is rotated with reference to the vertical axis to avoid superimposing the respective dots exactly on each other. They are printed so close to each other, however, that they give the proper color impression to the eye. When these half tones are printed in the respective colors and in proper register, they accurately reproduce in the resulting picture the color tones represented in the original. This is the four-color process commonly used for the best color printing.

The beauty and remarkable fidelity obtained in modern letterpress printing in halftone and in color depend very largely on the etching of engraved plates. The sensitivity of photochemical processes in reproducing detail and fine shadings on photographic paper is a frequent source of wonder, but we seldom stop to think that in letterpress printing these same delicate details, and exact color shades besides, are reproduced through the medium of etching metal plates with acid. The color etcher or "fine etcher" in the photo-engraving industry is one of the most highly skilled modern workers with metal. The color separations by means of color filters are not perfect, and corrections have to be made by the etcher to obtain exact color reproductions. The etcher does not work primarily for the depth of the dot in the photoengraving plate, although this also affects the printing quality. He works on the size of the dot. By a remarkable feat of imagination the etcher can visualize from the size of the dots as viewed through a magnifying glass in the different parts of the image on each of four copper plates, what the shade of the final print will be. He then adjusts the size of the dot accordingly by varying his etching procedure, or by burnishing.

As in type matter, the photo-engraved plates are usually not printed direct except for pulling proofs and for short runs. Duplicate printing plates are made by electrotyping or stereotyping, most usually the former.

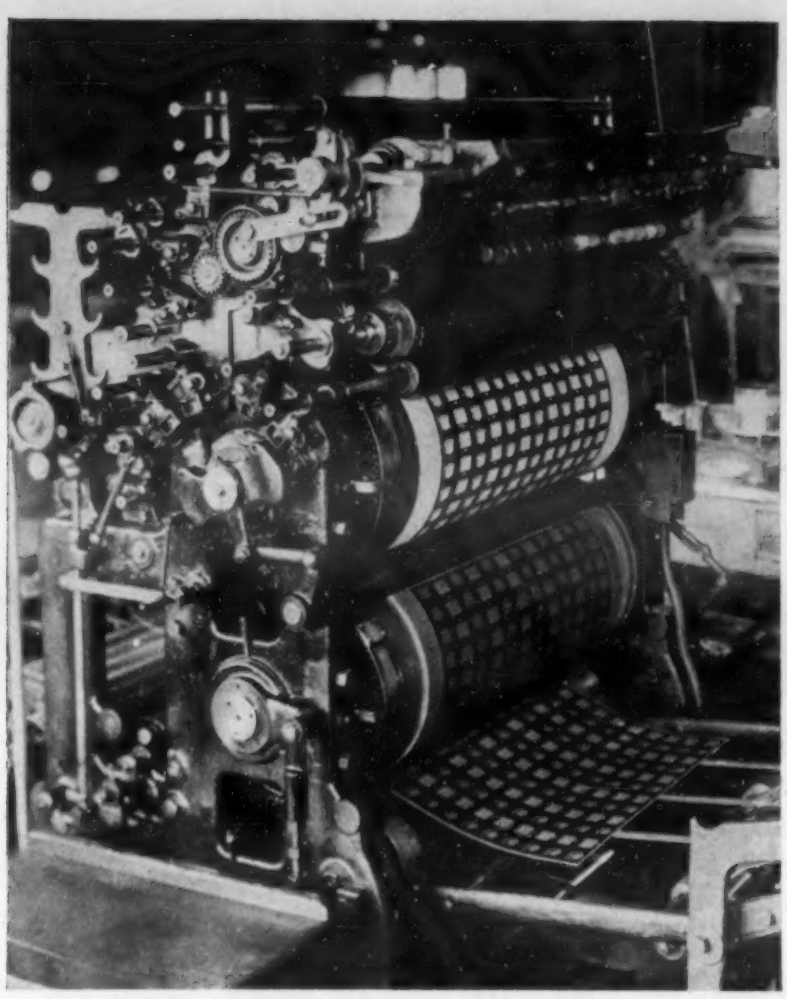
Photo Litho Camera Room. The first step in mechanically transferring an image onto a lithographic printing plate is to photograph it. This negative may be photographed to obtain a positive for correction which is in turn photographed onto the final press or proof plate. (Courtesy U. S. Bureau of Engraving and Printing).

LITHOGRAPHIC AND OFFSET PRINTING

IN lithography, the printing surface is a plane, as compared to relief or intaglio printing, no raised or hollow portions being present. In the recently perfected deep etched offset plates there is about 0.002 in. difference in level between printing and non-printing areas. The design to be printed is photochemically transferred onto a printing plate whereby the exposed portions will take and retain a greasy ink. Other portions are kept free from ink by keeping them damp with water. As the inking roller comes into contact with the moistened plate in printing, ink readily adheres to the previously inked lines or image, but is rejected by the surface which is damp. The process consequently depends upon keeping the ink and water from mixing, that is, differential surface tension.

As the name lithography implies, images were originally hand drawn on stone—an art that required a lot of skill, patience and experience. Metal printing plates are now used almost exclusively. Zinc and aluminum sheet are both well adapted for this purpose since they are inexpensive, easily handled and readily curved around cylinders for rotary printing. Zinc is often preferred because it is cheaper and considered by some to hold the image better than aluminum.

In preparing the plates for printing, the sheet metal is first "grained" by mechanical abrasion, such as by grinding or shaking with various abrasives (pumice-stone, emery, sand or flint) and steel, glass, wooden or porcelain marbles. This gives five or six times the original surface. The metal sheet is then sensitized, ready to receive the desired image by coating it with one of several different types of emulsions. Albumen, treated with ammonium bichromate, is quite commonly used, although bichromated glue, gum, and gelatine all have advantages for certain types of printing. The



Lithographed Tin Plate for Beer Cans. The rubber composition blanket is shown just above the tin plate. (Courtesy National Can Co.).

Offset Printing on Metal. The upper roll carries a grained zinc sheet on which desired images have been developed. It prints onto a composition rubber roll carried by the center roll which in turn prints onto the tin plate that is being passed through the press. (Courtesy National Can Co.).

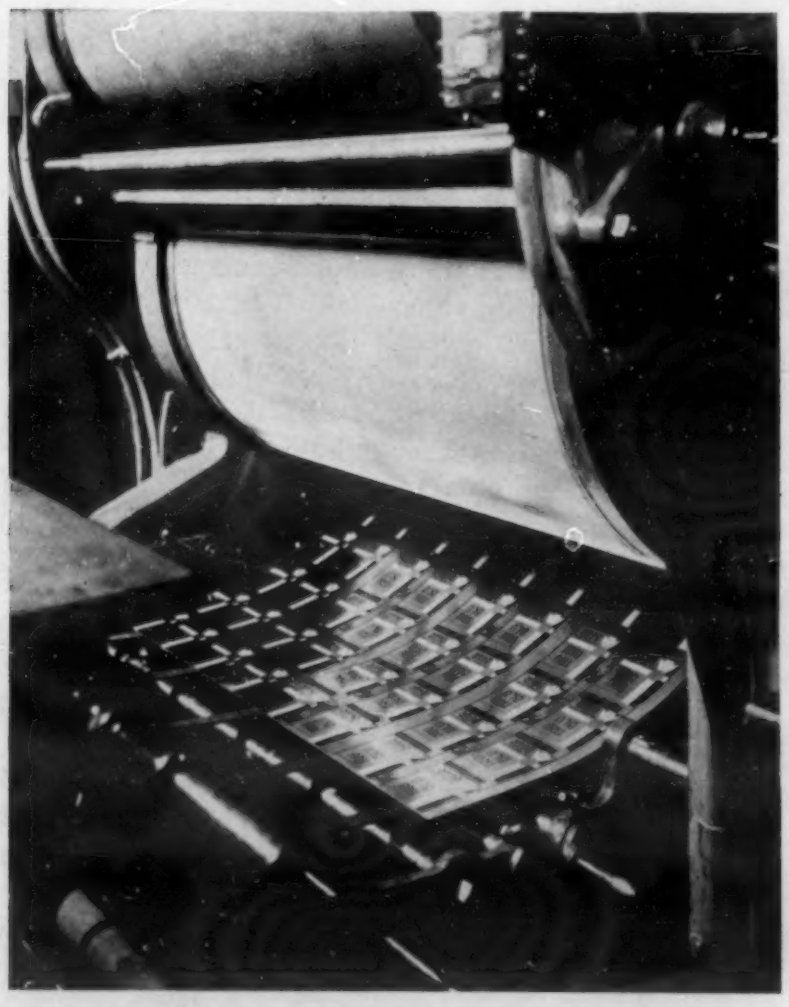


image is usually mechanically transferred to the metal plate by printing from a suitable photographic plate that has been corrected as to color and light values. (Transfer may be also effected by hand, using transfer paper.)

A greasy liquid developing ink is rolled carefully over the exposed plate and the whole washed with water, whereupon the ink remains on the exposed portions but is washed away with the soluble unexposed emulsion. After a slight etching the prepared plate is ready for use.

Most lithographic printing is done by the offset process rather than directly from the plates. In this method the image is first printed upon a steel cylinder covered by a rubber composition blanket. This in turn prints or "offsets" the image onto the material to be printed.

The offset process can produce very beautiful results of ordinary half tone and of color work as well as of type, although type is not so sharply printed as in letterpress because of the rubber blanket and because the image is reproduced photographically instead of by mechanical molding. Offset printing is especially well adapted for printing on soft and so-called art papers and for large posters where photoengravings and electrotypes would be more costly. For some other classes of work offset printing is cheaper than letterpress and the process has made heavy inroads upon letterpress printing. For the highest quality of printing, however, where sharp detail and accurate brilliant tone values and color reproduction are desired offset printing cannot as yet compete with letterpress printing from electrotypes. For publications there is still much uncertainty about offset printing and large periodicals cannot afford to take chances with it.

Metal Lithography

The printing and decoration of metals, especially of metal containers, is an important branch of lithography. Since sheet metal is too hard for printing by ordinary letterpress or by intaglio printing methods without injuring the type, offset lithography has been used almost exclusively for this sort of printing. Recently, the use of rubber plates in letter press work has opened possibilities in direct printing on sheet metal with many of the advantages inherent in the letterpress method, but rubber plates are not yet extensively used in this field.

Lithographic decoration of metal differs from printing on paper primarily in that the non-absorbent metal surface requires different drying conditions. Two types of ink are used—one that is similar to that used on paper and a "process" or high temperature type that becomes very hard on baking. It is normally necessary to bake one printed color, for example, before applying a second. Two color presses, i.e. two lithographing presses in tandem, are sometimes used for metal decoration when the colors do not overlap but it is sensitive work and not common practice. The paper lithographer deals principally in the primary colors and blacks. He can secure color effects by the blending of colors much more easily than the metal decorator. Until recently, each shade constituted a separate color in metal lithography. It had to be applied, the metal sheet baked for 10 or 15 mins. a

a temperature of about 220 to 250 deg. F., then another color applied. Thus, for some elaborate reproductions, 15 or more printing-baking cycles might be required. This has since been simplified to some extent by process work using primary colors but even now the use of 10 or 12 tints on high grade work is not uncommon.

Sheet metal is printed using the same general type of single lithographing press and offset blanket used in printing paper. Means are available for automatically feeding a sheet at a time, conveying it through the press then in an upright position through a tunnel oven for baking. Speeds of 3,000 sheets an hour of tin plate, for example, are common. Clean, black sheets as well as tinplate, terne plate and similarly coated sheets are readily printed in colors as well as in black and white. In general, any printing that can be done on paper can be favorably reproduced on sheet metal although not always as simply or easily as in paper printing. With the exception of extruded tubes, printing is always done on the flat metal sheet before forming. Usually the lithographed surface is protected and its beauty enhanced by coating it with a finishing varnish.

INTAGLIO PRINTING

IN the intaglio process the printing characters are etched or mechanically cut depressions below the surface of the plate. These depressions hold the ink and various tones are reproduced, not by varying the size of the hollows (as the size of the dots is varied in letter press and lithographic printing), but by varying the depth of the ink film they impart. Shadows which are cut or etched most deeply hold the most ink and lighter tones take ink proportionately.

Copper and Steel Engraving

Copper plate engraving and printing are one of the oldest methods of reproducing an image. The depressions are often made by hand with an engraving tool and obviously require considerable skill. Drawings, photographs, etc. are frequently transferred to the plate by photographic means and may be etched, then tool finished. Since copper plates can be used to print only several hundred or at most a few thousand copies and hardening or plating them has not come into common usage, for long runs the engraving is made on steel plates that are afterward hardened and sometimes chromium plated.

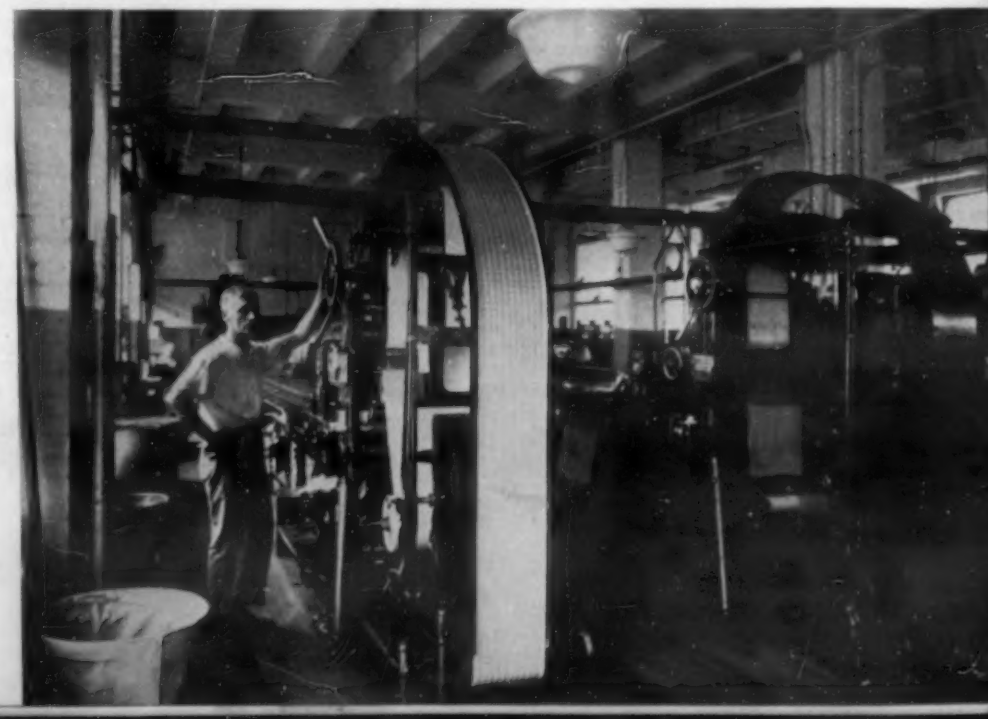
Steel and copper engravings give an excellent clean cut, sharp reproduction that is considered to be the finest type of printing. The method is limited to line work, however, and used largely in the black and white field or for some single color work. Although usually considered as being used only for wedding invitations and name cards, steel and copper plate and raised printing or die engraving are quite widely used in printing business as well as social stationery, paper currency, bank notes, bonds, certificates, postage and revenue stamps, and the like. A great advantage of steel plate engravings for printing valuable papers is the difficulty of duplication. Lithography also competes in this field.

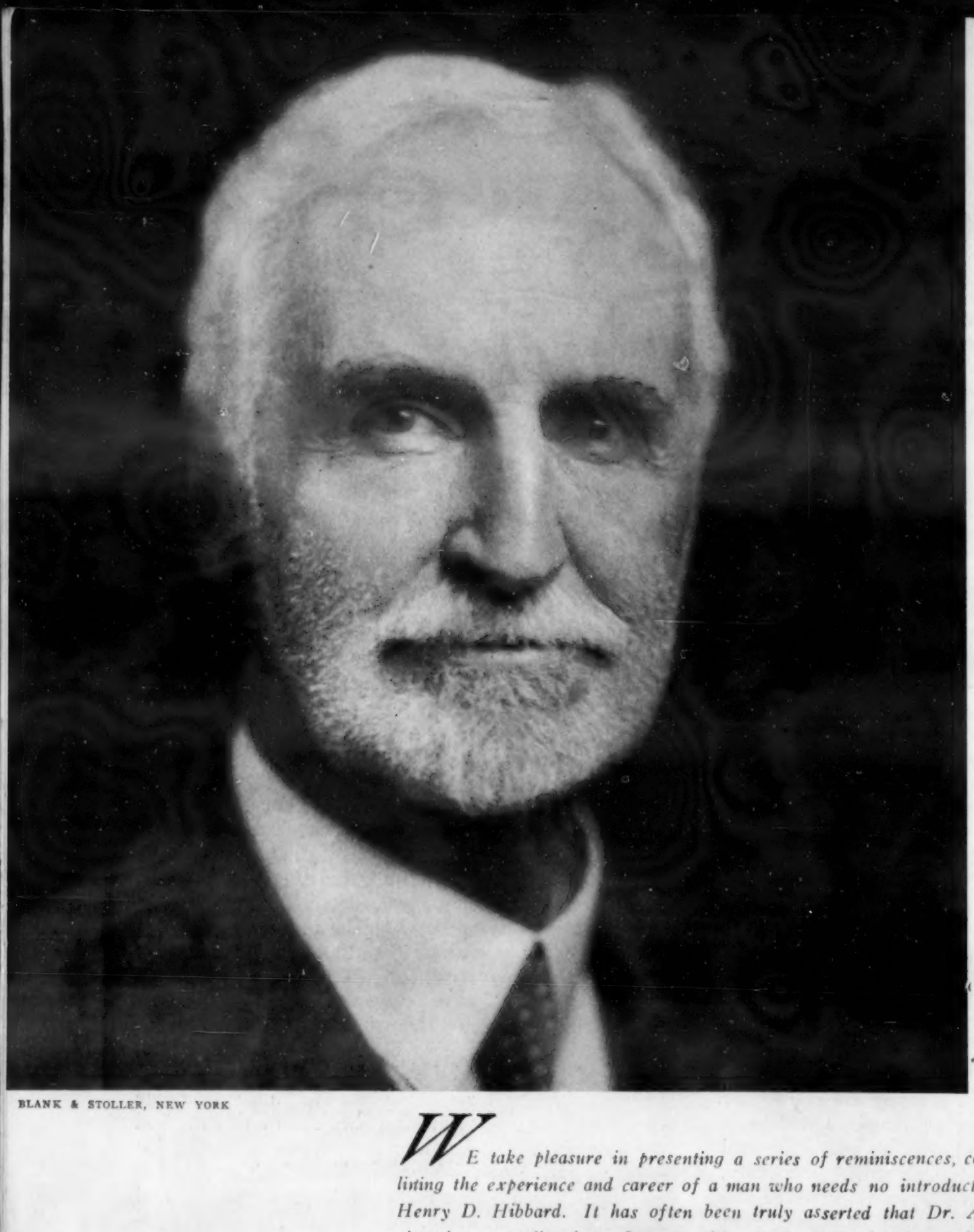
Gravure Printing

Intaglio printing from a copper cylinder on which the illustrations or designs have been etched are commonly designated as rotogravure, or rotary photogravure. From flat plates it is known as gravure. In reproducing a photograph for printing in this manner a screen is not required to break up the tone values. The copper or copper plated cylinders in rotogravure printing are etched with a series of uniform square cells for an entirely different purpose. During printing the cylinder is flooded with ink. The surplus ink must, therefore, be wiped from the relief non-printing areas. This is done by means of a thin steel knife (doctor blade), which leaves the margins clean and the cells filled with ink. If it were not for the uniform screen, therefore, the thin doctor blade would sink down and scoop out all the ink from the large dark printing areas called "solids." The same copper surface is used for type, line, and half-tone, all of these being transferred photochemically, and all being broken up by the same cell formation. It is one of the drawbacks of rotogravure printing that this cell formation can be noticed at the margins of type.

In transferring the image onto the copper cylinder for photogravure printing a transparent positive is first made and then a print on "carbon tissue" (paper coated with pigmented gelatine, sensitized with bichromate) which is transferred onto the copper cylinder. The gelatine image of the "carbon tissue" becomes more or less hard according to the light transmitted through the varying tones of the negative and thus holds back the ferric chloride etching solution so as to produce a varying depth. The use of the "carbon tissue" makes exact register for color work rather difficult. Photogravure also shares the disadvantage with lithography for color work that very little correction can be made on the printing plates themselves; tonal corrections have to be made on the negatives. Very good results are obtainable by gravure printing, however, both in black and white and in a wide range of colors and there is widespread use of this method for printing Sunday newspaper supplements and for some magazine and job work. Very high speeds are obtainable on the continuous roll presses used, and long runs may be made. Chromium facing of rotogravure cylinders and flat plates is frequently applied to obtain longer runs. *(To be Continued)*

Rotary Stamp Printing Press, 170 Subjects. (Courtesy U. S. Bureau of Engraving and Printing).





BLANK & STOLLER, NEW YORK

WE take pleasure in presenting a series of reminiscences, commencing with this issue, outlining the experience and career of a man who needs no introduction to many of our readers—Henry D. Hibbard. It has often been truly asserted that Dr. Albert Sauveur is the dean of American metallurgists. It can with equal appropriateness and truth be said that Mr. Hibbard is the dean of American practical steel men—men who for many years have been active in the actual production and study of steel making processes. Almost from the earliest days of the steel industry in this country, he has either been intimately connected with it or followed its development year by year. His reminiscences will more fully bear out these statements.

For some years Mr. Hibbard has been, and still is, a consulting engineer from his home in Plainfield, N. J. Born in Boston in 1856, he was graduated from M. I. T. in 1877. He has always been an active member of the A. I. M. and M. E. He delivered the Howe Memorial Lecture in 1928, taking as his subject, "Significance of Simple Steel Analysis." He is a member of the Legion of Honor of that organization, men who have been members for over 50 years.

Some years ago when, at the annual February meetings of the iron and steel division of the mining engineers, papers and discussions on live metallurgical topics and steel making problems were delivered by leading specialists and practical men—meetings which many of us remember as of outstanding merit and interest—Mr. Hibbard was a contributor not only of valuable papers on the manufacture and deoxidation of steel and on solid non-metallic inclusions, but also of wise counsel based on practical experience. He is still active in such matters.

A review of such a career, in the form of reminiscences, we are sure will be of keen interest and value.—E. F. C.

Steel Reminiscences—I

by Henry D. Hibbard

MY FIRST CONTACT with iron metallurgy occurred in 1869 when, with my brother and a cousin, older, who served as guide, I visited the plant of the Bay State Iron Co. in South Boston, Mass. It was indeed interesting and worthwhile even to me and also unforgettable, though details of the event are hazy. That company made puddled wrought iron, most of which, if not all, went into iron rails for railroads. The works were ably managed by Ralph Crooker, who was the first in this country, if not in the world, to roll 100 tons of rails on one mill in one day, which he did at the Bay State plant about the time of my visit or soon after.

One thing I remember about that visit was being astonished by the large sizes of the engines, as shown by their cylinders, which drove the rolling mills. That demonstrated the great power required for rolling metals. Some steel-headed rails were made at this works, but they were not wholly satisfactory. In any case they would soon have been supplanted by all-steel rails of Bessemer steel which was fast winning its place, though I had not then heard of it.

Mr. Crooker was, even in 1869, an old ironmaster. In 1826 he rolled the flat iron rails for the first railroad built in America. They were installed at the Quincy Granite quarry at Quincy, Mass. A part of that railroad is still there with bronze tablets telling its story. The immediate need of the railroad was the transportation to tidewater of the stone of which the Bunker Hill monument was built.

Crooker made those rails of 1826 in a tide mill located on what is now a part of Beacon Street, Boston. The power to drive the mill was supplied by tide water which flowed in and out of Back Bay, since then filled in and built over. That part of Beacon Street was called The Milldam by oldtimers even in my day. I well remember Back Bay through which the Boston & Providence R. R. ran on a fill. My home was in West Roxbury which was served by the Dedham branch of that railroad.

In the year of my visit, 1869, or the next, the first successful Siemens-Martin steel-melting furnace (open-hearth) in America was built at the Bay State Iron Co.'s plant. Its capacity was only five tons but, skillfully run by Archie Johnson as melter, it made marketable steel plates for boilers, rolled on a plate mill at the plant. In 1884-1885 I made steel at the Norway Iron & Steel Co. plant for that mill, of which more later.

My second ferrous foray was in 1876 when, as a student at the Massachusetts Institute of Technology, I visited with a classmate, the Bessemer steel plant of the Albany & Rensselaer Iron Co., at Troy, N. Y. There, for the first time, I saw steel made—a wonderful experience. As I remember, the steel made there all went into rails. When I first entered the steel business in 1879, this plant was one of eleven Bessemer steel works in this country. They all chiefly made rails, though some made other products also, which they classed as special steels. The Troy works were managed by the late Robert W. Hunt. In common with most eastern steel makers, this concern succumbed later to the competition of Lake ores and cheap coal of the west.

After leaving Troy we went to Port Henry, N. Y., and visited some of the iron mines there. Some of the ore went to the Troy works. In the mines we saw great faces of magnetite being worked. That was my first time underground in a metal mine, though I had been in a coal mine at South Joggins, Nova Scotia.

My first practical experience with iron metallurgy was at the Massachusetts Institute of Technology in 1878. The professor of metallurgy wanted to see if we could make iron in a little brick shaft furnace which was installed in the metallurgical laboratory. It was blown by a fan blower. The time was after I had been graduated but I helped in the trial as a volunteer. With Takuma Dan, a Japanese student of the Class of '78, I was assigned to do the charging which was done from a platform some feet above the general laboratory floor. Hence our experience came first.

The furnace was started and tapped once or twice but only one small pig of iron was obtained. The professor concluded that the shaft was too short—that the height of the charge was not enough for the iron to be reduced to metal before it reached the fusion zone. So the ore was melted only partly reduced.

After the furnace had been running a while, perhaps an hour or two, Dan walked off to one side and sat down on a box. I asked him why and he said that he didn't feel well. Then I began to feel queer, too. So I went down and told the professor how we felt and just then he noticed that he was not normal either. He knew what was the matter and said that the air was fouled by the furnace gases and that the trial would have to stop. The blast was taken off the furnace forthwith. Ventilation of the room was inadequate. Carbon monoxide manifestly escaped through the charging door, which was on the side of the shaft, and poisoned the air. That night I had the worst headache I ever had but the next day I was about normal.

(Continued on page 28)

Courtesy Bethlehem Steel Co.

Pouring a Large Ingot for a Heavy Forging

A FURNACE FOR

Treating Iron in Hydrogen

AT HIGH TEMPERATURES

by M. Gensamer and V. E. Thornburg

Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, and Westinghouse Electric & Mfg. Co., East Pittsburgh, Respectively

THE PREPARATION OF HIGH PURITY iron usually involves treatment of the iron in hydrogen at a high temperature to remove various elements present as impurities, notably carbon, oxygen and nitrogen. This requires a furnace which has a suffiicently large capacity and which is at the same time designed to minimize contamination of the iron. The handling capacity is determined partly by the size of the furnace and partly by the temperature of operation—the higher the temperature, the greater the output since the high temperature increases the rate of diffusion and hence reduces the time required for each treatment. The use of a high temperature, however, makes it very easy for contamination to occur, especially contamination with silicon, carried from refractories to the iron by the hydrogen.

Description of the Furnace

A furnace has been designed and used to treat iron in hydrogen in 3 to 5-lb. batches at temperatures up to 1450 deg. C. In this furnace there are no refractories in the specimen chamber; a sketch in cross-section appears in the illustration. The heating element, which is also the specimen chamber, consists of two concentric Armco iron tubes, A and B, which are joined mechanically and electrically at the bottom by the weld, C. Toward the upper end these tubes are spaced at D with a ring of asbestos board and sealed at E with a rubber gasket between copper flanges brazed to the tubes. The tubes are thus insulated electrically at the points D and E. A 10 K.V.A. transformer, F, having a single turn secondary, supplies the low-voltage, high-current power to heat the tube assembly through its own resistence. The current passes through heavy copper bars to the water-cooled copper blocks, G and H, which are clamped tightly to the machined surfaces of the two tubes. The tube assembly is placed in a steel can, I, and is fastened by bolting the flange, J, to the top of the can with an asbestos gasket seal. An aloxite brick wall, K, and granulated sil-o-cel, L, constitute the thermal insulation. The tube assembly can be replaced when necessary without disturbing the remainder of the furnace. One such assembly has been operated for a total of 16 weeks at temperatures above 1400 deg. C.

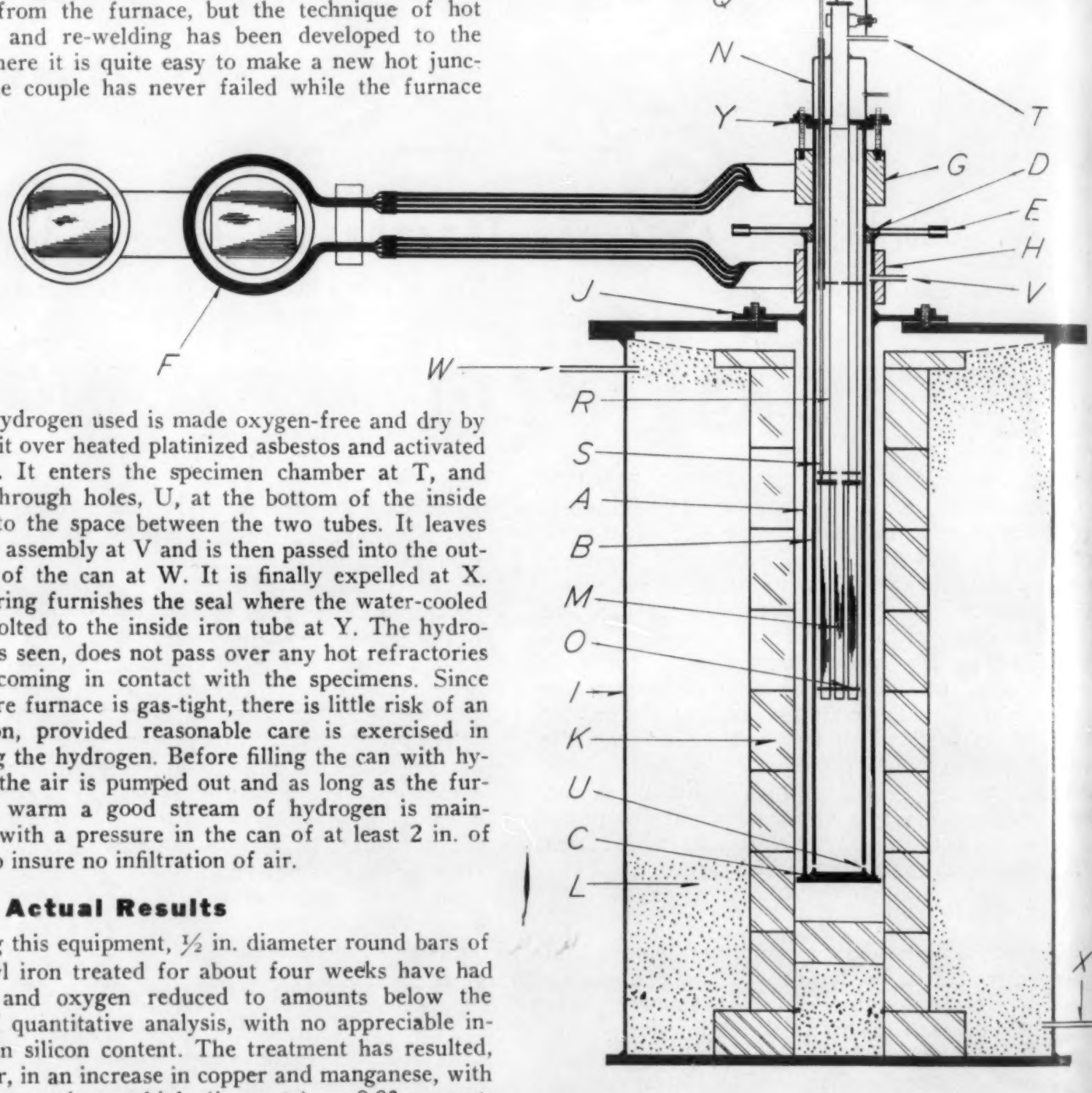
The specimens, M, are fitted into a neat bundle without touching each other by inserting them into drilled iron plates and are suspended in the inner tube from a water-cooled holder, N, in such a way that they are free to swing so that no considerable force can be exerted by the specimens on the tube wall in case of misalignment. Tiny pieces of pure magnesia are attached to the edges of these plates to prevent them from sticking to the walls of the chamber.

Measuring the Temperature

Provision is made for measuring the temperature with an optical pyrometer, by sighting on the bottom of the specimen assembly, O, through the prism, P, the glass window, Q, and the hollow tube, R. This temperature measurement has never been quite satisfactory because of the difficulty in achieving black-body conditions; iron in hydrogen at these high temperatures has a high emissivity. The use of an iron disc with a small hole placed above the specimen assembly to serve as a radiation screen has helped considerably. Experience in operating the furnace has provided an upper safe limit to the apparent operating temperature. This temperature is at least 50 deg. C. above the A_4 point of the specimen (as judged from the first appear-

ance of δ-grain boundary off-setting, a quite characteristic phenomenon), which places the operating temperature between 1400 and 1450 deg. C. and probably higher. This is high enough for quite rapid hydrogen purification.

The temperature is controlled by varying the output voltage of the transformer between an upper and a lower limit by means of a resistance in series with the primary. This resistance is shunted out when the temperature drops by a relay system actuated by a potentiometer-pyrometer. A tungsten-molybdenum thermocouple, S, has proved to be very dependable and generally satisfactory. It is usually broken in removing it cold from the furnace, but the technique of hot twisting and re-welding has been developed to the point where it is quite easy to make a new hot junction. The couple has never failed while the furnace was hot.



The hydrogen used is made oxygen-free and dry by passing it over heated platinized asbestos and activated alumina. It enters the specimen chamber at T, and passes through holes, U, at the bottom of the inside tube, into the space between the two tubes. It leaves the tube assembly at V and is then passed into the outer part of the can at W. It is finally expelled at X. A lead ring furnishes the seal where the water-cooled top is bolted to the inside iron tube at Y. The hydrogen, it is seen, does not pass over any hot refractories before coming in contact with the specimens. Since the entire furnace is gas-tight, there is little risk of an explosion, provided reasonable care is exercised in handling the hydrogen. Before filling the can with hydrogen the air is pumped out and as long as the furnace is warm a good stream of hydrogen is maintained, with a pressure in the can of at least 2 in. of water to insure no infiltration of air.

Some Actual Results

Using this equipment, ½ in. diameter round bars of carbonyl iron treated for about four weeks have had carbon and oxygen reduced to amounts below the limit of quantitative analysis, with no appreciable increase in silicon content. The treatment has resulted, however, in an increase in copper and manganese, with the copper going as high (in spots) as 0.03 percent, and the manganese to between 0.01 and 0.02 percent. In the original carbonyl iron, copper and manganese are very low. It is thought that this contamination arises from the fact that the tube assembly, which is also the reaction chamber, and the rods which support the specimens are made of commercial ingot iron. Nevertheless, the middle part of each bar is probably 99.97 percent iron (very conservatively it is at least 99.9% pure), which is quite satisfactory considering the size of the bars. By using thin sheets and lower temperatures, other members of the staff of the Metals Research Laboratory have treated iron from the same source and achieved a considerably greater degree of purity.[1]

Acknowledgment

The authors wish to express their thanks to the staffs of the United States Bureau of Standards and the Bell Telephone Research Laboratories who performed the chemical analyses discussed.

Reference

[1] C. Wells, R. A. Ackley, and R. F. Mehl, *Transactions*, American Society for Metals, Vol. 24, No. 1, March, 1936, pages 46-74.

Distortion Of Grains

BY FATIGUE AND STATIC STRESSING

by Charles S. Barrett

Member of the Staff of the Metals Research Laboratory and Lecturer in the Metallurgy Department, Carnegie Institute of Technology, Pittsburgh

TWO RATHER EXTENSIVE X-ray investigations of fatigue in metals have recently been carried out independently and concurrently. The author, with the cooperation of the X-ray and Fatigue Committees of the American Society for Testing Materials, conducted a research at the Carnegie Institute of Technology. At the National Physical Laboratory in England a study was made by Gough and Wood[2].

Certain experiments reported in these papers are directly comparable, and in these cases generally similar conclusions were reached. There is one question, however, of first importance from the practical standpoint, on which the investigations lead to different conclusions; this is the question of the effect on X-ray diffraction patterns of applying alternating stresses that do not ultimately lead to fracture.

Gough and Wood[2] concluded that with alternating torsion fatigue tests, X-ray diffraction patterns are essentially unchanged by stressing in the safe range, but that abruptly when the stress passes into the unsafe range the grains break down and the diffraction patterns are altered. Similarly, with alternating direct stresses, (tension and compression) they concluded that if the mean stress is zero, stressing in the safe range causes no change in structure that influences appreciably the nature of the X-ray spots, while stressing in the unsafe range alters the spots distinctly. Experiments in which the mean stress was not zero and the superior stress of the cycle was maintained at a constant value which exceeded the yield point, indicated that in the safe range of stress there is no progressive change after any initial change that occurs at the first application of the load, while in the unsafe range changes proceed to a degree dependent on the rapidity with which failure is approaching.

The author,[1] studying rotating beam specimens after stressing, concluded that alternating stresses in the safe range below the endurance limit produce changes in the diffraction patterns that are often of considerable prominence. Experiments were not undertaken to show whether these changes occurred only with the first application of the load or whether they were progressive changes, but it was emphasized that the nature of the changes in the safe range is the same as in the unsafe range, and that there is a gradual (not a discontinuous) increase in the degree of the changes as the stress level increases from one range into the other —at least when a large number of stress reversals has occurred. It was inferred from these results that the patterns do not register the damage to the material and do not permit a direct X-ray diagnosis of ultimate failure from fatigue. Any X-ray test to reveal actual damage in service or to predict probable life of a stressed component of a machine or a structure would be possible only if it were based on a comparison of patterns from the material in service with patterns from the same material stressed under laboratory conditions.

The practical importance of this point justified, it was felt, the additional fatigue experiments reported and discussed in the present paper, which were carried out using a special X-ray technique that is thought to be particularly useful for the purpose. These confirmed the author's previous conclusions. In the discussion is given a summary of numerous other experiments that are directly related to the problem and that also confirm the author's conclusions. A comparative study of grains that have been strained in tension is also presented.

The Method Previously Used

BOTH investigations referred to above used the same type of X-ray camera, a "back reflection" instrument in which a pinhole beam of X-rays is passed through a hole in the flat film, strikes a small area on the specimen, and is then diffracted back to the film at a high diffraction angle. Specimen and film are held stationary and individual grains of the specimen reflect the characteristic X-rays to form a ring of spots on the film. An estimate is made of the amount of blurring of these spots brought about by different stress conditions.

This method offers the advantage of yielding clear patterns with a short exposure, does not require the destruction of the specimen and does not require a specimen of special shape. A disadvantage of the method, however, is that it surveys a very limited number of

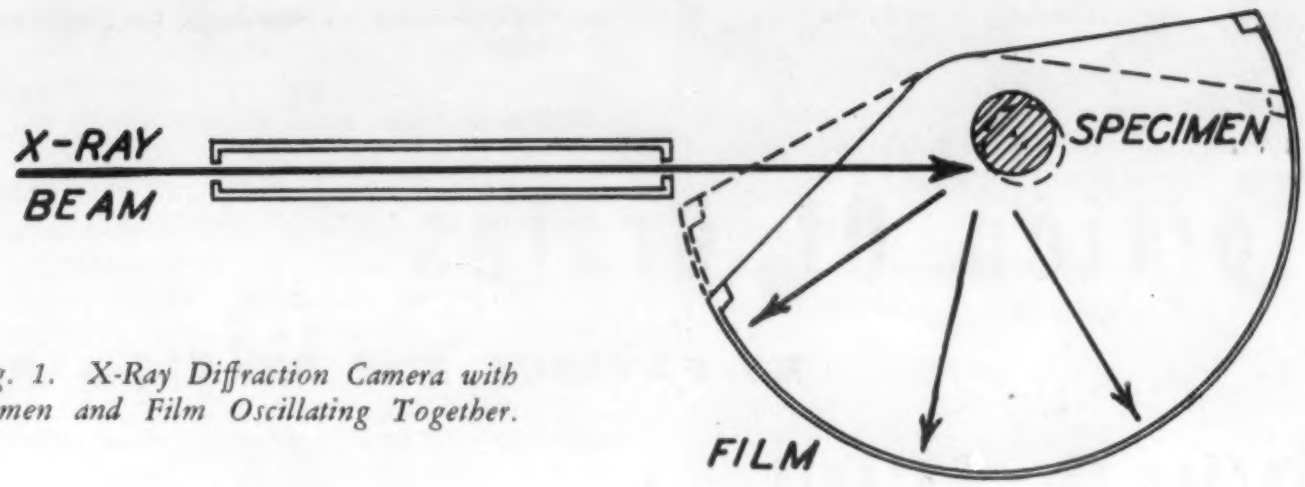


Fig. 1. X-Ray Diffraction Camera with Specimen and Film Oscillating Together.

grains—only those grains so oriented as to reflect the characteristic X-rays to some point on the Debye rings. In the fatigue studies in question, only one or two rings of about an inch in diameter were used. In such cases it is necessary to avoid as much as possible the overcrowding of the rings with spots, for this causes spots to overlap and become confused. On the other hand it is necessary to avoid having too few reflections to indicate the average condition of the grains. While the number of spots is under control by varying the size of the area struck by the X-ray beam, a suitable adjustment that avoids these extremes is not always reached and the sensitivity of the test is lowered thereby.

Gough and Wood have given a formula by which the change in orientation of a reflecting plane may be calculated from the elongation of a spot. The formula applies, however, only to the elongation in the direction of the circumference of the Debye ring, and shows only one component of the distortion of a grain—the one that corresponds to the widening of a spot in the peripheral direction. A more complete picture of the nature and amount of the distortion or "dislocation" of a grain is desirable.

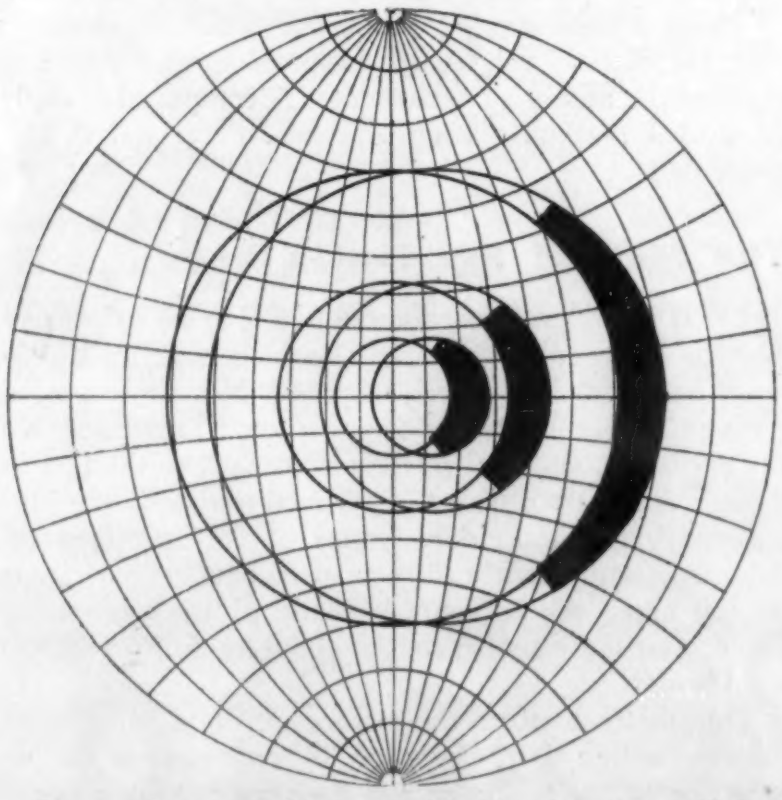


Fig. 2. Stereographic Projection Showing Areas Charted in Figs. 3, 4 and 5.

An Oscillating Film Method

THE method introduced below is considered to be an improvement over the stationary film technique because it replaces the Debye ring with a band of considerable width and thus permits a large number of spots to be registered without overcrowding. It is, in effect, a method by which a series of diffraction rings are laid side by side, each being taken with a slightly different position of the specimen. The data from a band of diffraction rings can be plotted on a stereographic projection to form a "pole figure." Ordinarily a pole figure is plotted by preparing a series of photograms of the stationary type, with the specimen rotated a few degrees between each, but the present problem is more conveniently handled by a camera[3,4] in which the film and specimen are mounted on the same carriage and oscillated together through a small range of angles as indicated in Fig. 1. The film exposed in this way is then itself a portion of a pole figure (somewhat distorted) and reveals the spreading of spots in all directions.

It has the further advantage of indicating, through the relative density of the different portions of a distorted spot, the fraction of a grain having any given orientation. Comparing this oscillating film method with the Laue method, it will be noted that the density distribution in a distorted Laue spot (an "asterism" streak) is altered by the intensity distribution in the general radiation spectrum and by the efficiency of the photographic emulsion for the different wavelengths, whereas in the present method the whole picture is formed by X-rays of constant intensity and wavelength. With the method employing monochromatic radiation with stationary specimen and film, each spot may be described as a section through the corresponding Laue streak, while the camera of Fig. 1 provides effectively a continuous series of adjacent sections through these striae, revealing their true distribution. Or, stated in terms of a pole figure, the stationary film technique reveals the density along the circumference of a circle (the reflection circle), on the pole figure, and the oscillating film arrangement of Fig. 1, by sweeping the reflection circle over the projection, reveals the density distribution over an area.

Most of the patterns of the oscillating type presented in this paper are taken under conditions where the K_α doublet is so close that it may be regarded as a single spot. This simplifies the interpretation of the patterns.

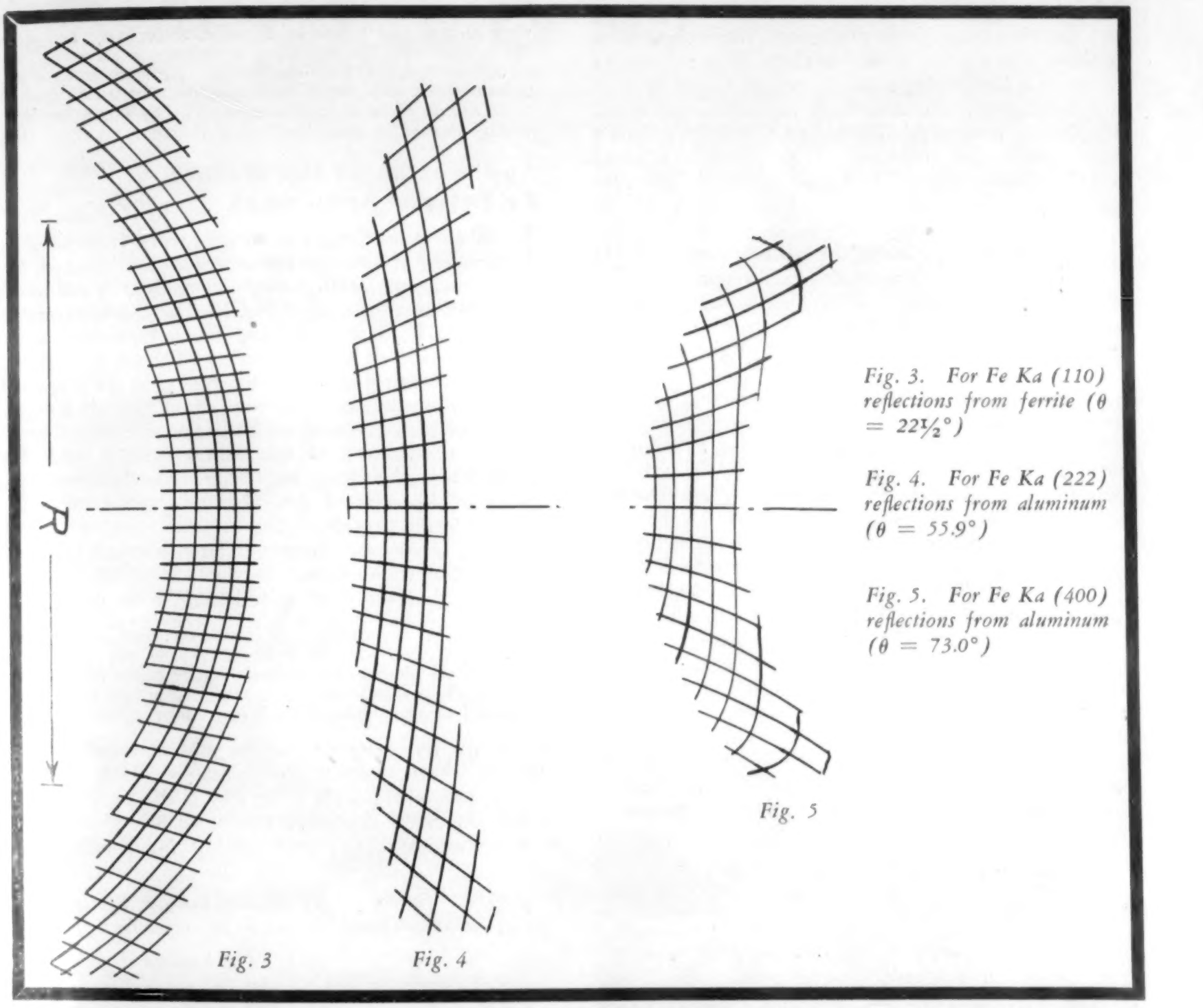


Fig. 3

Fig. 4

Fig. 5

Fig. 3. For Fe Ka (110) reflections from ferrite ($\theta = 22\frac{1}{2}°$)

Fig. 4. For Fe Ka (222) reflections from aluminum ($\theta = 55.9°$)

Fig. 5. For Fe Ka (400) reflections from aluminum ($\theta = 73.0°$)

Figs. 3, 4 and 5. Charts for Interpreting Patterns Obtained With the Camera of Fig. 1. Ruled with 2-deg. Intervals. Scaled to fit Figs. 7 to 10.

Charts for the Oscillating Film Method

It is possible to transfer each of the spots on a film exposed as in Fig. 1 to a stereographic projection and thus to draw a pole figure showing the "preferred orientation" for a reflecting grain. A more convenient procedure, however, is the reverse, the mapping of latitude and longitude lines from the stereographic projection upon the film or upon a chart to be superimposed on the film. The angular spread of each spot may then be estimated directly by eye.

Charts for this purpose are presented in Figs. 3, 4 and 5. They are drawn for a cylindrical camera whose radius is indicated by the dimension *R*, or for a film enlarged the amount that would be necessary to bring the camera radius up to this dimension. The charts are drawn with the equatorial line (perpendicular to the axis of rotation) as the dot-dash center line, the lines of constant latitude as the horizontal curves and the meridians of constant longitude as vertical curves. Both latitude and longitude lines are drawn at 2 deg. intervals. The charts and oscillating film patterns in this paper are printed at the same magnification, and may be directly compared. To make the charts more generally useful, however, they were made to cover oscillations up to 10 deg., whereas the X-ray patterns shown here were produced with only a 5 deg. oscillation of film and specimen.

The charts were constructed by the following graphical method: On an accurate stereographic net the reflection circles were drawn for Fe Kα radiation reflecting from (110) planes of Fe ($\theta = 28\frac{1}{2}$ deg.) and from (222) and (400) planes of Al ($\theta = 55.9$ deg., 73.0 deg.) respectively. One reflection circle was drawn for each of these planes with its center in the center of the net, as shown in Fig. 2. Each reflection circle was then rotated 2, 4, 6, 8, and 10 deg. in turn and plotted, (only the first and last appear in Fig. 2). Areas on the stereographic projection that were enclosed in this series of reflection circles and that were needed in the interpretation of the films—the black areas in the figure—were then mapped to form the charts of Figs. 3, 4 and 5.

To do this, radial lines were drawn at 2 deg. intervals on the stereographic projection; the intersections of these with a given reflection circle were mapped as points on a Debye ring after the manner used by Wilson[5] in constructing charts for X-ray orientation work, the angles around a Debye ring being Wilson's angle *a*. Since each successive 2 deg. rotation of the film shifts the Debye ring on the film, a series of these Debye ring coordinate points was laid down, each ring of points displaced appropriately from the first in the equatorial direction. Finally, the latitude and longitude lines of the film chart were drawn through these coordinate points to correspond with the manner in which the latitude and longitude lines on the stereographic net pass through the intersection points of the reflection circles and radial lines.

Different charts are required, of course, for each combination of wavelength and reflecting plane; Fig. 3 is for Fe K*a* radiation on Fe (110) planes, and Figs. 4 and 5 for Fe K*a* on Al (222) and (400) planes respectively. Copied on transparent film and superimposed on the X-ray patterns, these charts enable an immediate estimation of the distortion of reflecting planes of a grain in terms of angular displacement. It will be seen from the charts that areas having an angular spread of 2 deg. in latitude by 2 deg. in longitude are almost equiaxed in the neighborhood of the equator but that they are somewhat elongated at the extremities of the charts. This is reflected in the X-ray patterns as a tendency of spots to elongate into streaks when they occur at positions removed from the equator. It is interesting to note, however, that the distortion of the nets in Figs. 3, 4 and 5 is very much smaller than the distortion of corresponding nets used with the Laue method.

Note: Nets for the Laue method have been published by J. Leonhardt, *Zeitschrift für Kristallographie,* Vol. 61, 1925, page 100; these and E. Schiebold's nets are reproduced in "Internationale Tabellen für Bestimmung von Kristallstructuren," Vol. 2, Bortraeger, Berlin, 1935, pages 633-637.

Fig. 6 is a reproduction of a film obtained on the apparatus sketched in Fig. 1. The four strongest bands of spots are, from left to right, (110), (100), (211) and (220) reflections of Fe K*a* from a rod of Armco iron recrystallized at 950 deg. C. for 5 minutes. The background fog in this type of photogram is relatively greater than in one taken with a stationary film because the exposure times are longer, and with some materials only the lower order reflections retain enough contrast, after deformation, to be useful. Therefore, only those bands showing clearly the structure of the spots have been reproduced. These are enlarged to a size to fit the charts and to show more clearly the details of the spots.

Fig. 6. Type of Pattern Obtained with Camera of Fig. 1. Recrystallized Armco specimen.

Note: The radius of the film was 44.6 mm., the pinholes were ¾ mm. and 1 mm. in diameter, respectively, and were separated 80 mm. The exposures were made on a tube operating self-rectifying at 35 kilovolts, with care taken to have the pinholes filled with radiation. Exposure times varied from 4 to 12 hrs. at 10 to 20 milliamperes. The Fe target was frequently cleaned to minimize general radiation.

Application of the Method To Fatigue Specimens

THE effect on the grains of cold work from fatigue stressing at different stress amplitudes is shown by the following series of photograms made with the oscillating film arrangement of Fig. 1. The specimens were of the R. R. Moore rotating beam type, and after stressing were etched to a sufficient depth to remove the cold work introduced by machining in the preparation of the specimen. A portion of the surface at maximum stress is compared, in each case, with a portion of the surface of the same specimen near the grips, where the stress amplitude is much lower (reduced in the ratio of the cubes of the specimen diameters in the two places).

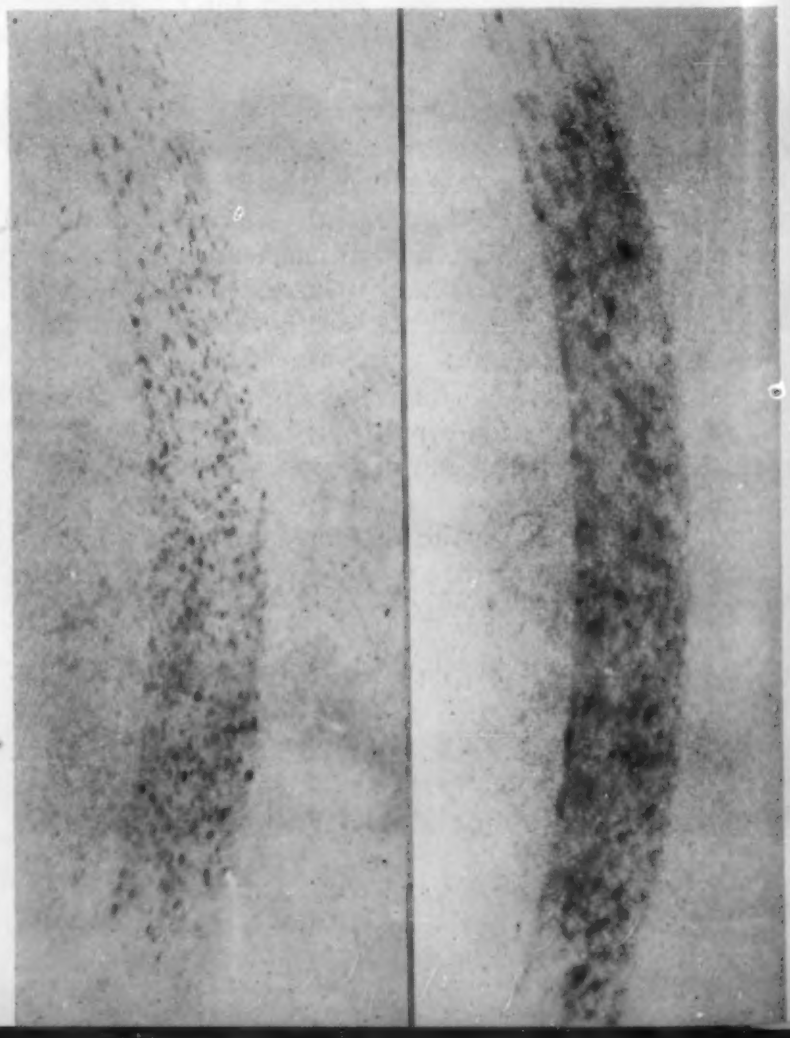
In Fig. 7 are reproduced patterns from a structural silicon steel whose endurance limit is 47,000 lbs. per sq. in., and whose yield point is 66,700 lbs. per sq. in.

Note: The analysis of the specimen was as follows: C 0.36, Mn 0.77, Si 0.34, P 0.047, S 0.040 per cent. The S-N curve is given in the author's earlier paper (See reference 2). This sample and the others used in this study were stressed 1 to 3 yrs. prior to the X-ray study.

On the left (Fig. 7a) is the pattern from a point that had been stressed approximately 30,000 lbs. per sq. in, and on the right (Fig. 7b) is the pattern from the point under maximum stress, 48,000, (just above the endurance limit) representing the condition of

Fig. 7. Patterns from Broken Fatigue Specimen of Structural Silicon Steel. Fe Ka (110) reflections.

(a) Unstressed area. *(b) Stressed slightly above the endurance limit for 2,987,100 Cycles.*



the metal 2 mm. from the fracture, which occurred after 2,987,100 cycles. Every spot in the maximum stress pattern appears to have been distorted to some extent, and a large number have been blurred so much that their overlapping has produced a nearly continuous darkening in the band.

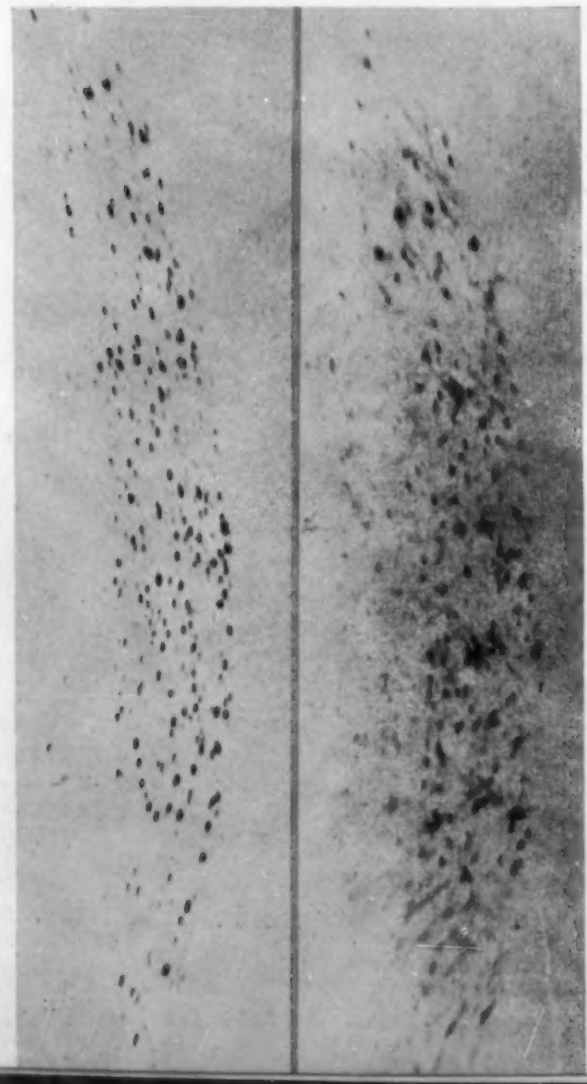
Fig. 8 is a study of the cold work produced by stressing below the endurance limit. The specimen was an annealed plain carbon steel containing 0.85 per cent carbon, with mechanical properties as follows: Endurance limit 34,500 lbs. per sq. in., proportional limit 21,000, yield point 36,500, tensile strength 85,000 lbs. per sq. in., elongation 36 per cent, and reduction in area 61.6 per cent. At the left is shown the pattern from a point near the grips, stressed at 21,000 lbs. and at the right the pattern from the area under maximum stress, 33,500 lbs. per square in., after the specimen had withstood 18,000,000 cycles without breaking and after the surface layers, disturbed by machining, had been etched away. Figs. 8 and 9 may be compared with related patterns, made with stationary specimen and film, that have been reproduced in the earlier paper.[1]

As in the preceding figure, spots are seen which have become blurred or elongated in one or more directions. The large proportion of the spots thus distorted—roughly a third—is evidence of a considerable amount of cold work below the endurance limit.

An even more pronounced example of distortion of grains when stressed in the safe range of stresses is shown in Fig. 9. The specimen in this case was of annealed commercial aluminum, 2S-0, with a yield point of 3,150 lbs., an endurance limit of 5,000 lbs. per sq. in., and a composition of 99.2 per cent Al, with minor impurities of Cu, Si and Fe. The stressing was done in a rotating beam fatigue machine of the R. R. Moore type. Patterns are reproduced for (a) a portion of

Fig. 8. Patterns from Annealed Steel Fatigue Specimen (0.85% C) After It Had Withstood 18,000,000 Cycles.

(a) Area at low stress level. *(b) Area stressed just below endurance limit.*



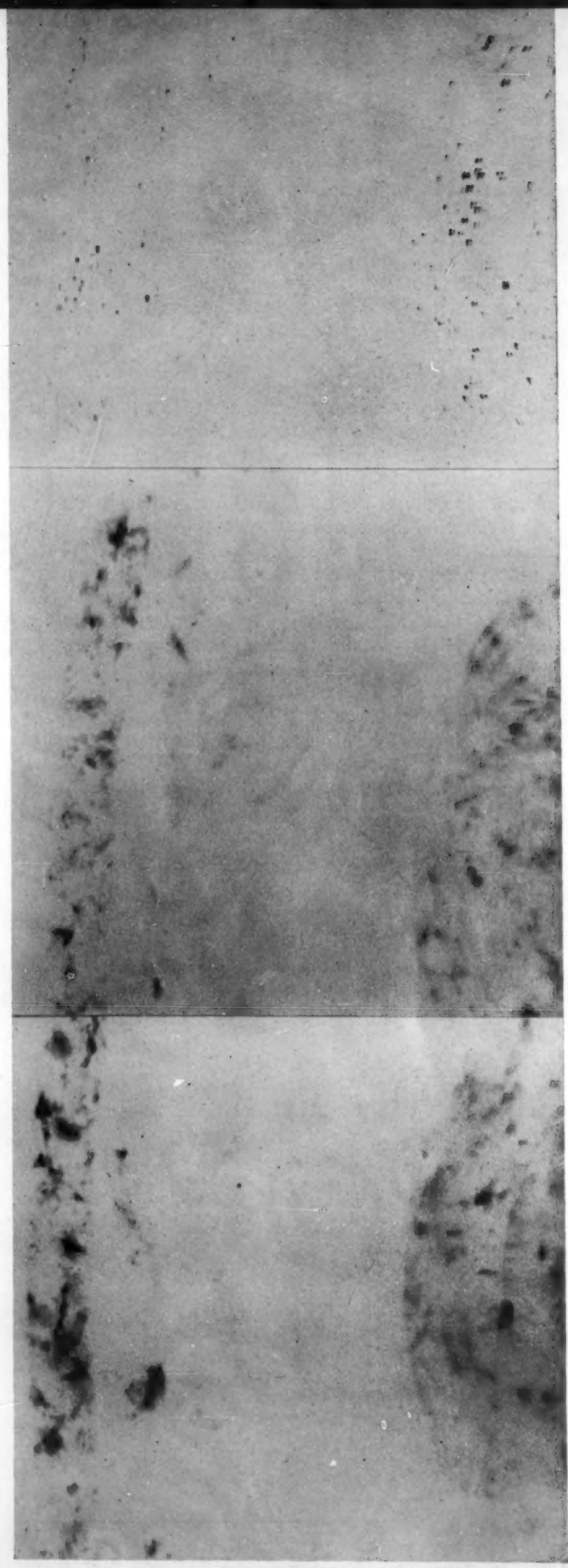


Fig. 9. Patterns from Aluminum (2S-O) Fatigue Specimen After It Had Withstood 505,000,000 Cycles. Fe Ka (222) and (400) reflections.

(a) Unstressed area.

(b) Stressed at 3,500 p.s.i. (below endurance limit).

(c) Stressed at 4,000 p.s.i. (below endurance limit).

the specimen at zero stress, prepared by sectioning, polishing, and etching the specimen and exposing the point at the center of the cross section; (b) a portion of the etched outer surface that had been stressed at 3,500 lbs. per sq. in., and (c) the central point on the etched outer surface where the maximum stress had been 4,000 lbs, per sq. in. The specimen had withstood 505,000,000 cycles without failing. Practically 100 per cent of the grains have become distorted here without leading to a failure.

An Application to Static Stressing

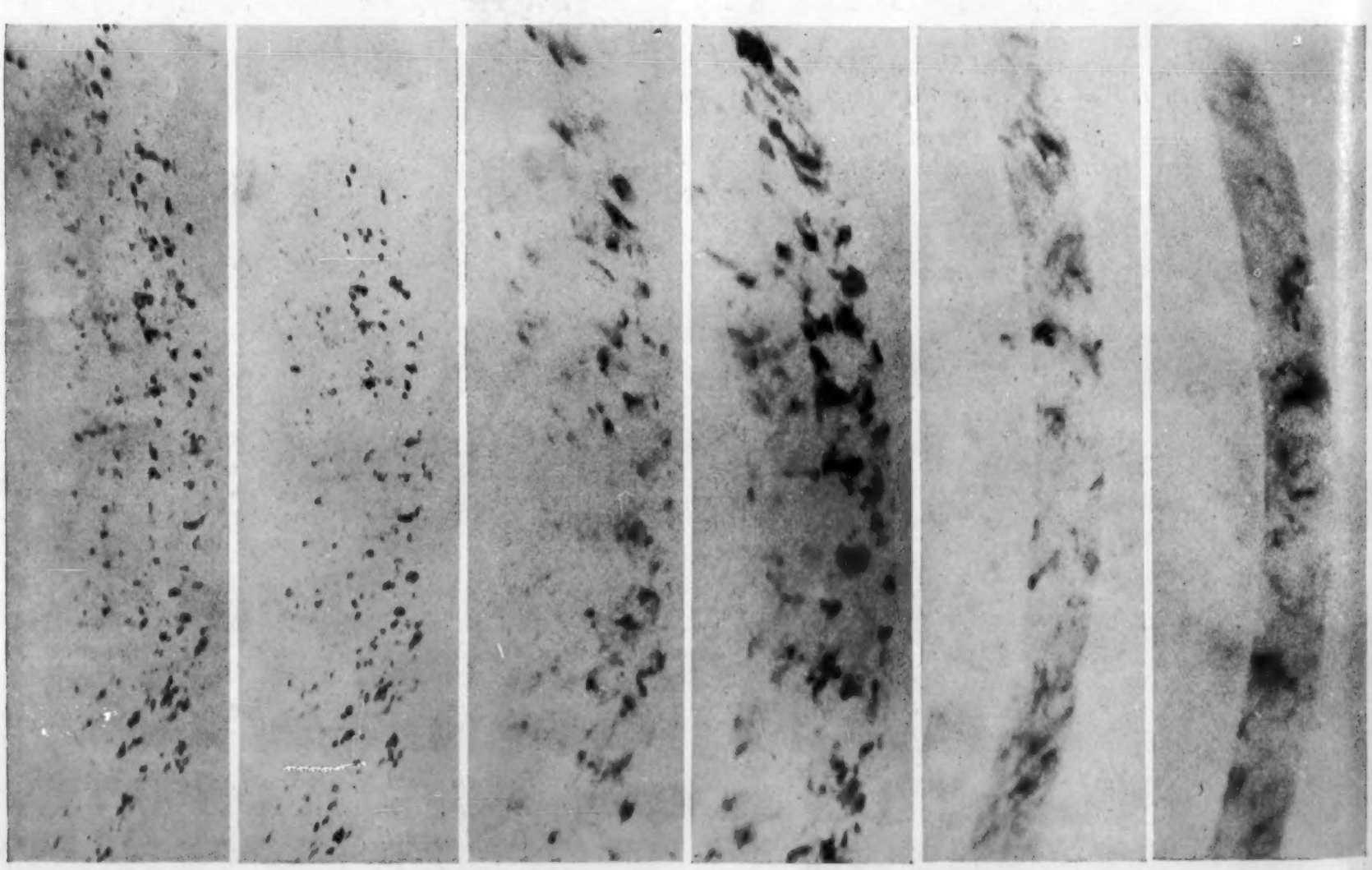
THE progressive changes in the diffraction pattern with increasing elongation in tension are shown in Fig. 10. A recrystallized Armco iron rod ¼ in. in diameter was pulled in a tensile machine to the total elongations given in the figure, measured on a 2 in. gage length; the specimen was removed from the machine and mounted on a special jig in the X-ray camera after each successive elongation. Reflections from identical grains were registered in the first two films of this series, but in subsequent exposures the beam struck areas slightly displaced from each other and the films do not show identical reflections.

The similarity of the 0.25 per cent elongation pattern with the 0 per cent pattern is due to the phenomenon of Hartmann (Lüders) lines: The particular spot struck by the X-ray beam did not lie within an area undergoing deformation and forming a Lüders' line.[6] A progressively increasing spreading of the spots is shown, the spots becoming less dense as a consequence of their covering greater areas on the film, and overlapping with neighboring spots to build up a nearly continuous background. (The 3.3 per cent film is abnormally black in comparison with the others because of a longer exposure time.) Details of the structure of the spots will be discussed later.

As an illustration of the points mentioned above in the discussion of X-ray methods, Fig. 11 is presented, showing the effect of these elongations on the Debye rings formed with stationary film and specimen. The same specimen, pinholes, camera and radiation were used as before, but with the carriage clamped in one position. A relatively small number of spots appear, and these spread only around the Debye ring because of the small divergence of the primary X-ray beam. They indicate that only a small proportion of the spots are distorted at 1.8 and 3.3 per cent elongation, and that practically all are distorted at 6 and 10 per cent.

The radial widening of Debye lines from cold work is a matter of considerable interest, since it signifies a distorted lattice in which either the microscopic internal stresses are large, or the lattice is fragmented into crystallites so small (10^{-5} or smaller) as to lack resolving power for the X-ray beam. A series of photograms, Fig. 12, showing the line widening vs. per cent elongation was therefore taken for comparison with Figs. 10 and 11. A common criterion for line width, the state of resolution of the $K\alpha$ doublet, was used. This dictated the choice of a set of reflections occurring at high diffraction angles where the dispersion is large, and a slight oscillation of the specimen during the exposure to permit a given grain to reflect both components of the doublet. The photograms were

Fig. 10. Patterns from Recrystallized Armco After Successive Elongations in Tension as Indicated. Fe Ka (110) reflections.



0% *0.25%* *1.8%* *3.3%* *6.0%* *10.0%*

made on a stationary cylindrical film with Fe Kα radiation reflecting from the (220) planes. It will be seen that the blurring of the doublet begins to appear in some grains at 3.3 per cent elongation, spreads to most of the grains after a stretch of 6 per cent and includes all the grains by the time the elongation has reached 10 per cent.

Discussion

Deformation of grains in fatigue: X-ray studies of the oscillating film type as well as the previously reported stationary film studies[1, 2] fail to reveal any difference in the mechanism of deformation of grains whether the deformation is brought about by fatigue stressing in the safe range or the unsafe range or by static loading. The deformation results in all cases in a rotation of parts of a grain with respect to each other about a single axis or, more generally, about several axes in an approximately random manner. The range of orientation increases with the stress level in fatigue stressing and with the elongation in the tensile stressing, gradually reaching a state in which there is insufficient material of any given orientation to give a strong X-ray reflection to a limited spot on the film.

In view of these results there can be no question but that the X-ray patterns reveal a distortion of the crystal lattice by plastic flow of the metal along slip planes, and that on the average the distortion is practically the same as in the static case. It is known[7,8] that slip bands formed by fatigue tend to appear wider than those from static loading, but this appearance is due to the tendency of lines to group more closely together in fatigue than in static loading so that high magnification is required to resolve the numerous components of what appears to be a single line at low magnification[9]. If such differences in distribution of planes of slip bring about differences in the microscopic or submicroscopic distortion of the grains, the X-ray experiments have failed to show them.

Strictly speaking, however, this conclusion applies only to the average conditions in a polycrystalline material, in which the slip interference at grain boundaries plays an important part, and in which slip in many grains must have occurred on two or more slip planes in the lattice. There still remains the possibility that, in tests with single crystal specimens so arranged as to avoid the disturbing influences of grain boundaries and duplex slip, the X-ray would reveal some differences between static and fatigue tests in their distortion of the grains.

That slip takes place during fatigue tests in the safe range of stress as well as in the unsafe has been shown in numerous other ways. Slip lines appearing on a polished surface have often been observed during stressing in the safe range.[10] Gough has emphasized the similar appearance of the lines irrespective of the stress at which they form. Internal stresses such as are produced by quenching have been shown to be relieved by applying alternating stresses with amplitudes in the safe range [11, 12], an event that definitely points to plastic flow, since it occurs at temperatures well below those at which recovery or recrystallization would be anticipated. Stressing under the endurance limit also produces other indications of cold work in some materials. For example, the indentation hardness of a stressed specimen is increased in some instances just as it is above the endurance limit[13, 14]; the endurance limit is raised in some materials[15]; and in many cases during the initial stages of stressing the specimen is heated more than can be accounted for unless mechanical hysteresis from plastic flow is assumed.

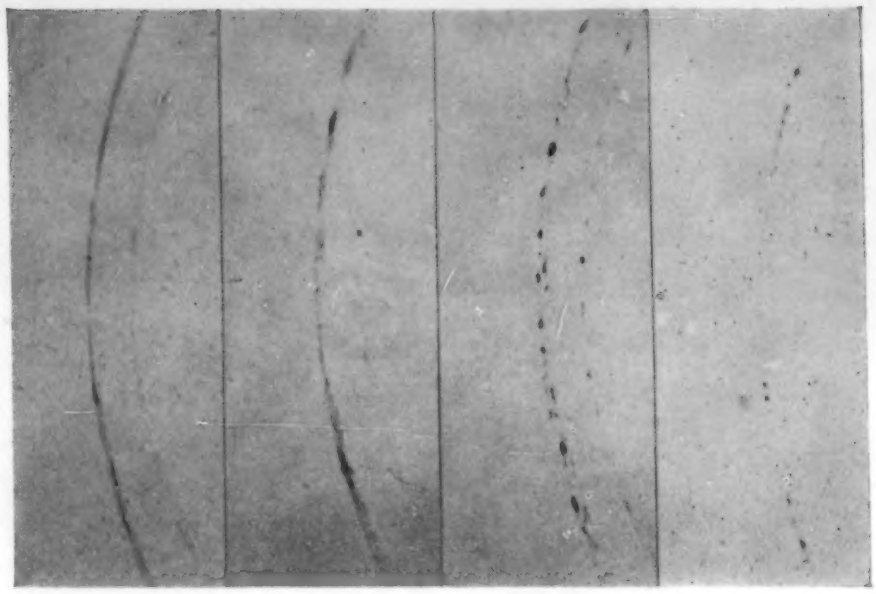
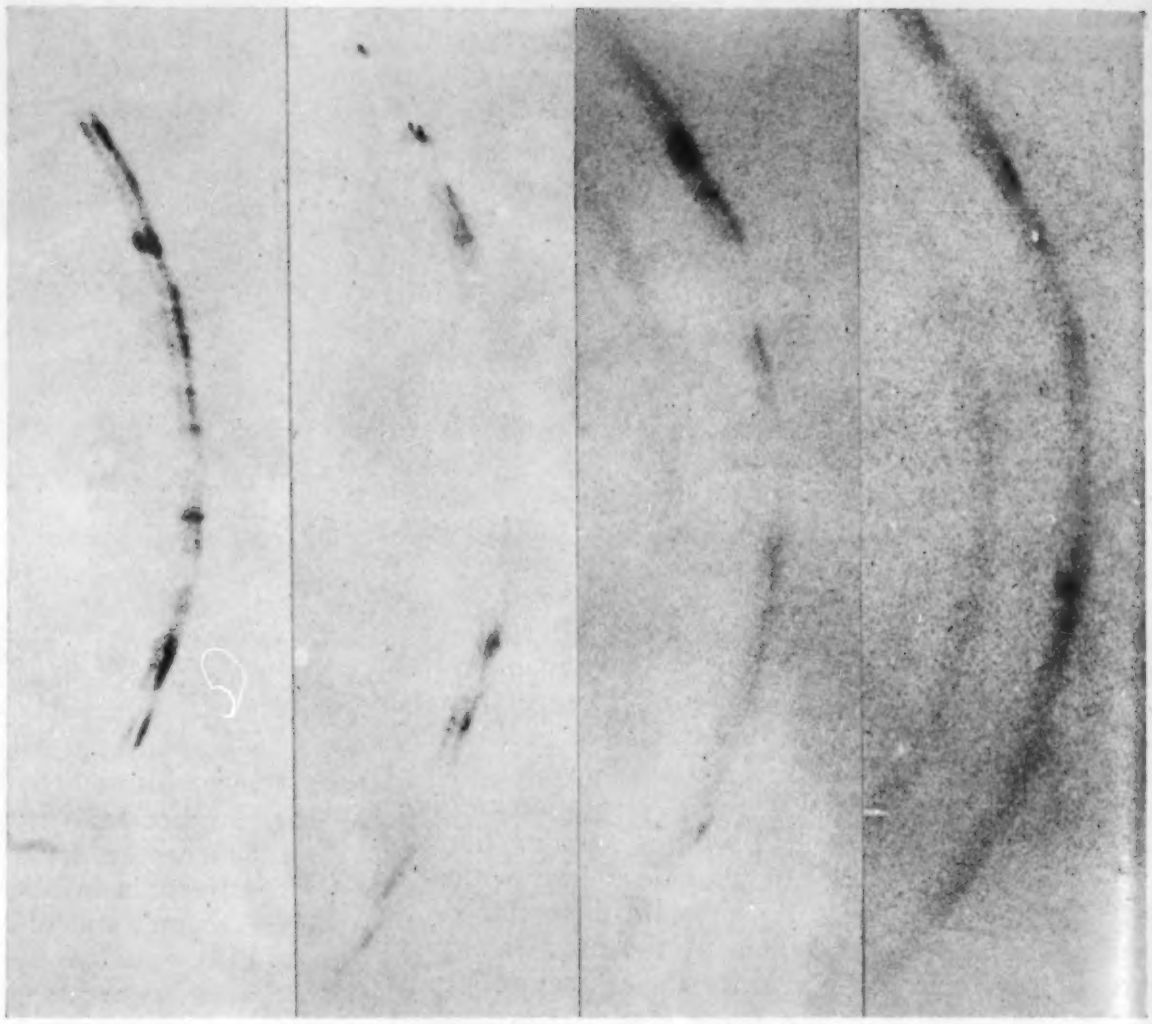


Fig. 11. Ordinary Debye Patterns (stationary specimen and film) for Same Experiment as Fig. 10. Fe Ka (110) reflections.

With general agreement among workers that slip frequently occurs in the safe range and may be recognized by numerous methods such as those listed above, it is pertinent to inquire as to the sensitivity by which it is recognized in the X-ray method compared with the other methods. The principal limitation of the X-ray method is that it is suitable only for annealed materials[1]. While the available data are rather too meager for an exact comparison, a study of the literature gives one the impression that in this class of materials the X-ray is more sensitive to flow than some of the methods and less sensitive than others. "Heat bursts,"—transient evolution of heat during the early stages of cycling—might well have indicated flow where Gough and Wood's diffraction patterns failed to give clear evidence of it. This is suggested by the fact that Gough and Wood failed to find any progressive effect after the first cycle of loading (unless the range of stresses was above the endurance limit) whereas wide hysteresis loops and marked heat evolution have been found for hundreds of thousands of cycles or in some cases for millions of cycles in the safe range of stresses.

In any event the question is not one of prime importance in practice, for once it is accepted that the X-ray diffraction is to be correlated with cold work rather than with spreading cracks or other progressive damage (and there now seems every reason to believe that it should be thus classified), the X-ray must take its place with all other tests of the same category. With materials that are cold worked appreciably by fatigue at and below the endurance limit a test based solely on the X-ray would probably be in error "on the safe side," underestimating the endurance properties of the material, while in materials where failure can occur with little or no evidence of cold work,[20] the X-ray would tend to overestimate the endurance of the material, just as the other related tests would.



1.8% 3.3% 6.0% 10.0%

Fig. 12. High Angle Diffraction Lines Showing Progressive Widening with Elongation in the Same Experiment as Fig. 10. Fe Ka (220) reflection [also Fe Kβ (310) faintly shown.]

Deformation of grains in the tensile test: Gough and Wood[2] have come to the conclusion, by studying the spreading of spots on their stationary film back reflection photograms, that either static or dynamic stressing produces three effects:

1. Dislocation of normally perfect grains into parts tilted 2 deg. or less from the original orientation.
2. Formation of crystallites of 10^{-4} to 10^{-5} cms. in size with a wider orientation divergence.
3. Presence of lattice distortion such as to produce radial line widening.

On the basis of the photograms shown in the present paper, there appears little justification for distinguishing process (1) from (2). Judging by Figs. 9 and 10, for example, the distortion of a grain proceeds by a reorienting of the parts with respect to each other by bending or perhaps by fragmenting. The range of orientation increases continuously with the increasing severity of the cold work and does not appear to be limited at any stage to 2 deg. While there are few spots to be seen that correspond to ranges of as much as 5 deg. in these figures, it must be pointed out that the greater the area covered by a spot the weaker it must appear; highly distorted spots are not seen as entities but merely serve to increase the background darkening. In consequence of the overlapping of spots the background becomes more and more continuous as increasing numbers of the spots contribute to it.

There seems no need for postulating that grains first tend to break into a few large fragments slightly tilted with respect to each other, then in some other way to fragment into 10^{-4} cm. crystallites with greater orientation divergence. On the contrary there is more reason to expect a gradual spreading of spots, if one considers the numerous experiments on the deformation of single crystals, for in the vicinity of the slip planes local rotation occurs that increases gradually with the amount of shear [21,22] and, in addition, increased bending and buckling result from slip interference at the grain boundaries.[23,24,25] Inasmuch as the average grain deforms by slip on several slip systems and is itself surrounded by several grains slipping in various ways, the axes of bending or rotation must be numerous, spreading the X-ray reflections in more than one direction, as a rule.

Gough and Wood[2] seem inclined to the view that fracture under static stressing is associated with a limiting amount of dislocation and lattice distortion. It should be pointed out, perhaps, that this statement cannot be extended to different materials, to a given material after different heat treatments, or to different conditions of loading or to different temperatures of deformation. That is, the amount of reorienting of grains and the amount of line widening that comes about before fracture are influenced by the numerous factors that influence the stress-strain curve of a material. Ludwig and Scheu's experiments[26] have been among the most conclusive with respect to line width. (A review of the experiments and controversies on the subject has been included in the earlier paper.[1]) They have shown that the line width at fracture is different with different types of loading and prior heat treatment, and that the width at a brittle fracture also differs from the width at a ductile fracture.

One interesting experiment showed that an air-hardened steel gave wider lines in the unloaded state than the same steel did when annealed and then loaded to the breaking point. Neither can a definite amount

of rotation of grains be assigned to a fracture stage. This follows from the fact that the development of a preferred orientation in a deformed piece is directly related to the amount of elongation or reduction in cross section that has occurred in the deformation process. In the tensile test, for example, there is much less opportunity for a well defined preferred orientation to develop before failure than there is in the case of rolling or wire drawing.

While the experiments reported here are incapable of adding much to the present knowledge of the crystallographic nature of the slip process or the mechanism of generating preferred orientations, a few points should be discussed. The spots do not show a tendency to elongate preferentially toward the nearest intensity maximum that would appear on a photogram showing the equilibrium preferred orientation for the tensile deformation. This is in accord with the fact that in the tensile structure there are actually an infinite number of orientations in which a grain should be in equilibrium. In consequence, a given spot in the diffraction pattern might move in almost any direction and yet be caused by reflection from a grain whose lattice was rotating toward one of the equilibrium orientations.

A comparison of Figs. 10, 11 and 12 suggests that line widening is going on simultaneously with the reorientation process, increasing as the reorientation proceeds, rather than following after an advanced stage of the breaking up of the grains as is concluded by Gough and Wood[2]. This implies that coincident with the spreading in orientation of parts of a grain, there is either an elastic bending of lamellae (microscopically distributed internal stresses) or a reduction of the grain to crystallites smaller than 10^{-5} with insufficient resolving power to give sharp lines. It remains uncertain which of these factors is to be regarded as the major contributor to the increased line width. (The question is discussed and references given elsewhere.[27])

Summary

CONSIDERABLE plastic flow can occur by fatigue stressing in the safe range of stresses under the endurance limit. This was concluded from X-ray photograms previously published by the author and is confirmed by the present series, made with a different type of camera in which the specimen and film are oscillated in synchronism. It is contrary to the conclusions of Gough and Wood, but is in accord with the results of other methods that detect plastic flow during fatigue stressing.

Charts are presented by which films of the oscillating type may be interpreted in terms of the range of orientation of portions of a grain. The photograms indicate that the lattice of a polycrystalline grain is progressively distorted into wider ranges of orientation when it is subjected to increasing elongation in tension or increasing stress amplitude in fatigue, and that the diffraction lines simultaneously become wider.

Acknowledgments

The fatigue data and previously stressed fatigue specimens used in this study were kindly furnished by R. E. Peterson of the Westinghouse Electric & Mfg. Co. and by R. L. Templin of the Aluminum Co. of America.

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THE PROCESS AND RESULT OF

Austenite Transformation

AT CONSTANT TEMPERATURE

A Contribution from the Research Laboratory
United States Steel Corp., Kearny, N. J.

FOR A STEEL OF EUTECTOID composition there is a characteristic equilibrium temperature (the so-called Ae_1 point in pure iron-carbon alloys) above which the steel will remain for an indefinite time in the austenitic state, and below which the austenite is unstable and tends to transform. When however a steel, previously rendered austenitic, is held at a constant temperature level below this limiting temperature, the transformation is not instantaneous but requires for its onset and for its completion definite periods which are characteristic, for a given steel, of the temperature level at which the steel is being held.

The most convenient way to depict what happens is by a temperature-time diagram with a logarithmic time scale, for the process requires periods ranging from a second or less to a month or more, depending upon the temperature level at which the steel is held and upon the composition of the steel. Such a diagram was constructed, on the basis of experimental observation of the rate of transformation of a eutectoid steel at a series of constant temperature levels, on a large scale (the original being about 6 ft. by 4 ft.) and embellished with micrographs, at an original magnification of 2500 diameters, showing the structure of the products of the transformation at various temperatures; this is reproduced, on a scale about one-third the original, in the large illustration accompanying this general description and brief discussion of the diagram.

On this diagram there are, at any temperature level below the characteristic equilibrium temperature, three time zones:

(1) that in which the austenite, though unstable, persists as it has not yet begun to transform; this zone, which lies above and to the left of the left-hand curve, is marked by an idealized austenite structure;

(2) that in which the transformation proceeds, at constant temperature, to completion—the shaded band between the two S-shaped curves;

(3) that in which transformation is complete, and the structure and properties of the treated steel definitely set; this lies to the right of the right-hand curve.

The micrographs between the pair of curves show the structure, (against a martensite light background) characteristic of the temperature level, of what has transformed when the transformation has gone halfway; those to the right the corresponding structure when transformation is complete. The series of micrographs illustrate how change in actual transformation temperature brings about a graded difference in structure of the finished product, hence of its properties as shown by the hardness numbers (both in Brinell and in Rockwell C units) which appear beside the corresponding micrograph.

There are two temperature ranges within which the transformation is rapid, one in the vicinity of 1000 to 1100 deg. F., the other below about 200 deg. F.; and two ranges within which the transformation is slow, one at temperature levels just under the equilibrium temperature, the other between about 700 and 250 deg. F. In other words, by choice of the temperature level, the steel may be caused to transform very rapidly or quite slowly; and the resulting structure—that is, the mode of dispersion and distribution of the products (ferrite and carbide) of the reaction—is definitely characteristic of the temperature level provided that the steel is held there long enough to permit it to transform completely at that level.

At the highest temperatures, the product consists of coarse lamellae of ferrite and carbide; at lower temperature levels the pearlite becomes progressively finer until at about 1000 deg. F., when the transformation is fastest, it is practically unresolvable even with the highest power lens. At lower temperature levels, where the transformation is less rapid, the ferrite-carbide product has a needle-like or acicular form, as contrasted with the rosette-like or nodular form characteristic of temperatures somewhat higher. At temperature levels below about 100 deg. F. the reaction is a different one and is rapid; the carbide is now not precipitated at all, but is retained in the unstable, supersaturated, solid solution called martensite.

The general form of the curve representing the zone of transformation is the same for all steels hitherto investigated, the level of fastest transformation apparently being not more than about 300 deg. F. below the temperature at which the austenite ceases to be stable. But the position of the curve on the time scale depends markedly upon the composition of the steel. Any alloying element (including carbon) which can be put in solution in austenite delays the onset of

transformation and retards its progress, thus displacing the pair of curves to the right. Moreover, the effect of an alloying element is quite specific, as indicated by the following data on the period required for the onset of transformation at the temperature level at which this period is a minimum, for a series all containing about 0.50 per cent carbon and another element as noted:

0.5%	manganese	less than 1 second
1.0	manganese	about 1 second
2.0	manganese	about 10 second
4.0	manganese	about 400 second
4.0	nickel	about 2 second
13.0	chromium	about 300 second

The occurrence of the transformation is also influenced by the austenite grain size, other things being equal, larger grain size always retarding the process. For instance, for a single steel which had previously been heated to different temperatures in order to establish a series of grain-sizes, the minimum period required for half-way transformation was about 2 sec. for grain size 8 to 9, 3 sec. for size 7 to 8, 10 sec. for size 4 to 5, and 15 sec. for size 2 to 3. Such differences, and the specific effect of alloying elements, raise many questions which will not be answered except by systematic investigations of the process and mechanism of the crystalline transformation of steels; we shall therefore not discuss them here.

The Significance of Constant Temperature Transformation Rate to Heat-Treating Practice

If we plot a cooling curve for a specimen cooled from a temperature at which its austenite is stable, and superimpose on the diagram a series of such continuous cooling curves, they will intersect the curve representing the onset of transformation somewhat as shown in Fig. 2.

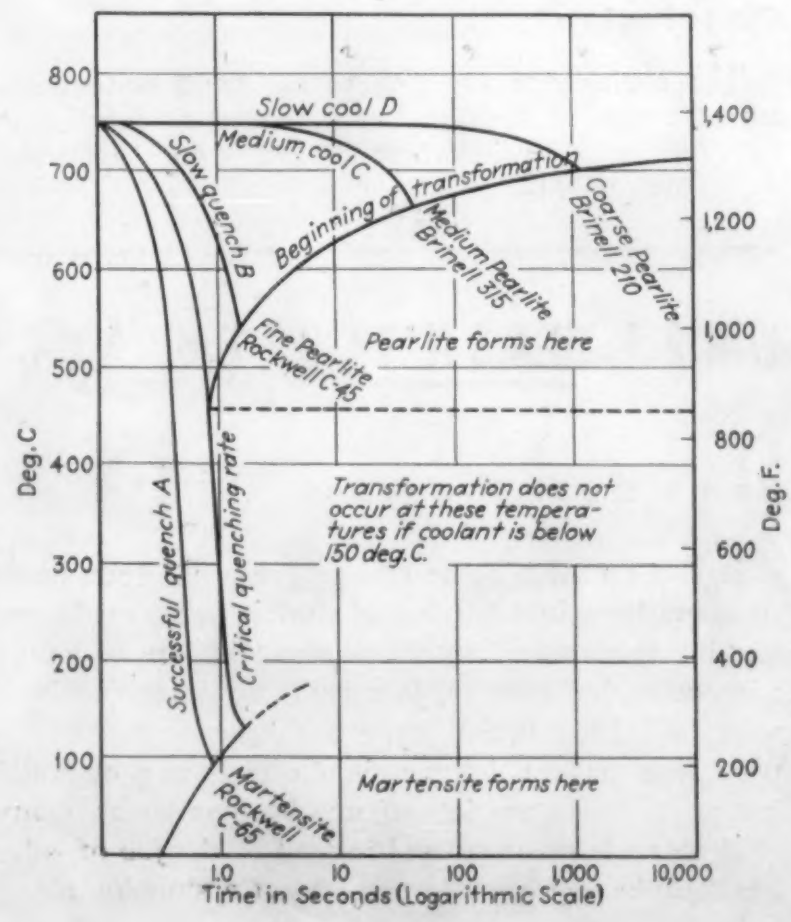
Note: The curve for onset of transformation with falling temperature is not strictly identical with our experimental curve which is for a series of constant temperature levels; but the difference is slight and can generally be neglected in practice.

Very slow cooling results in transformation largely at relatively high temperatures within which range the product is coarse pearlite of comparatively low strength and hardness and of high ductility. The faster the rate of cooling the more the transformation is depressed to a lower and lower temperature range, and consequently the product is of the finer pearlitic type of higher hardness and strength and lower ductility. At some cooling rate the continuous cooling curve fails to intersect the upper portion of the S-shaped curve, and in that case the steel will transform to hard martensite when, in its continued cooling, it reaches the lower region of high transformation rate near room temperature. Thus we see at once why carbon steel has to be cooled rapidly (quenched) in order to harden it; such cooling for hardening must be drastic enough to clear the upper region of rapid transformation near 1000 deg. F. if transformation to the softer pearlitic structures is to be prevented.

At intermediate rates of cooling the transformation will occur partly within the higher temperature range pearlite and partly in the lower range to martensite; this is commonly referred to as the "split" transformation. This condition is always encountered in the quenching of heavier sections in which the surface hardens fully to martensite while the core transforms to the softer pearlitic products, because of the unavoidably slower cooling of the interior; in the intermediate zone between the hardened surface and the soft core, mixtures of martensite and fine pearlite will be formed as the result of the "split" transformation at intermediate cooling rates prevailing there. In any ordinary cooling schedule the conditions bringing about transformation within the range 950 to 300 deg. F. will not be encountered. In order to get such structures the steel must be rapidly cooled to the desired temperature level, and then be held there long enough for the transformation to progress to completion. Carbon steel, heat-treated in this manner, possesses a rather unusual combination of ductility, strength, hardness and resistance to fatigue; this mode of heat treatment has been discussed elsewhere.

Since an alloying element displaces the transformation curve to the right, it follows that, for a given cooling rate through the appropriate Ae_1 temperature, an alloy steel will actually transform at a lower temperature than a carbon steel, and therefore have the properties corresponding to that lower transformation temperature. Indeed we may state that if a group of low-alloy steels of the same carbon content are all made to transform completely at a single constant temperature, the resultant structures will be very similar and the products will differ but little in properties from one another. The fact that an alloying element does, by delaying the transformation, bring about a lower temperature of transformation under usual heat-treating schedules, accounts for the higher hardenability of alloy-bearing steels. Moreover this delay, particularly in the temperature zone of fastest transformation, permits a rate of cooling of an alloy steel which could not be used on a carbon steel without

Fig. 2



1400
1300
1200
1100
1000
900
800
700

1
10
10^2
10^3

AUSTENITE (STABLE)

Ae1 TEMPERATURE

AUSTENITE (UNSTABLE)

1225°F

BHN 293
RC 31

1150°F

BHN 352
RC 37

1075°F

BHN 388
RC 41

1000°F

BHN 401
RC 42

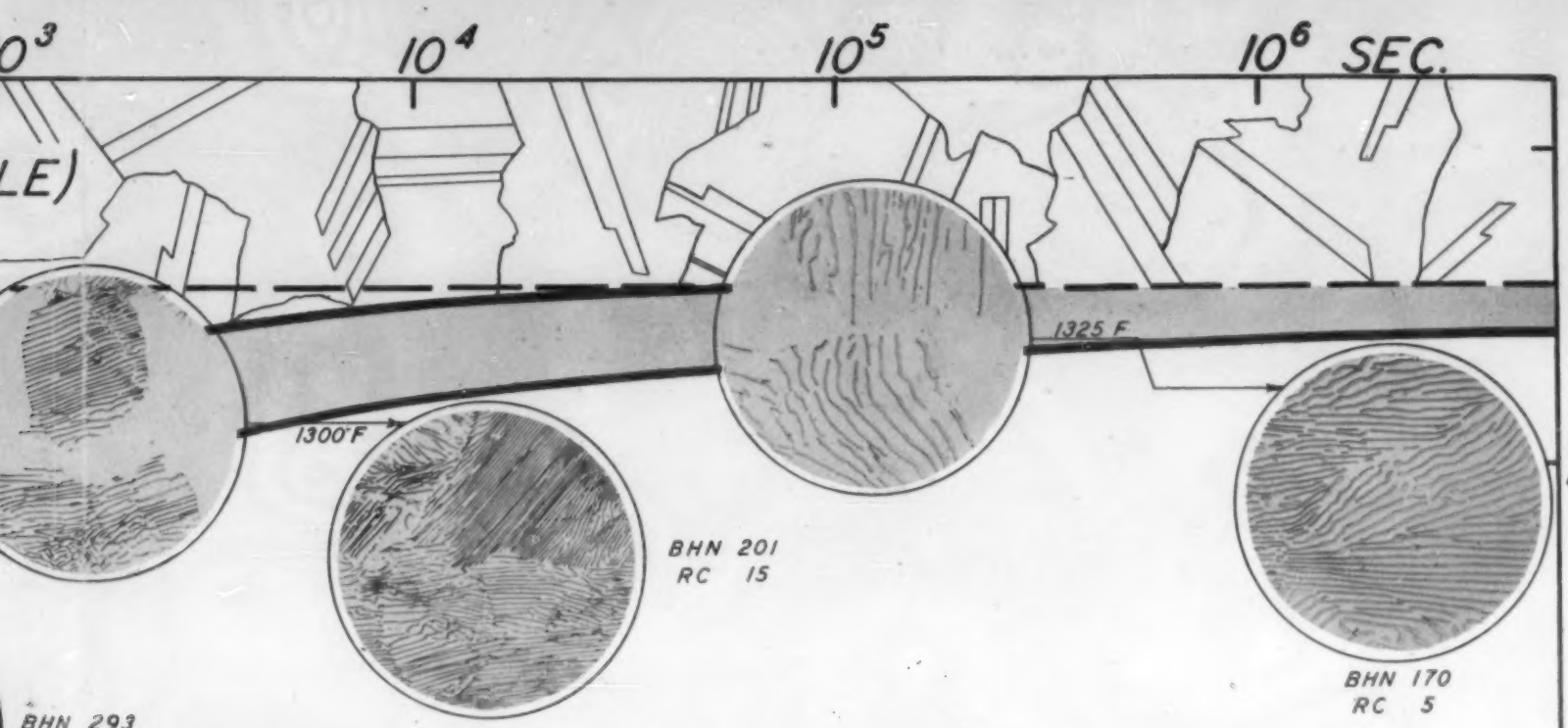
925°F

BHN 401
RC 42

850°F

BHN 388
RC 41

750°F



THE PROCESS AND RESULT OF AUSTENITE TRANSFORMATION AT CONSTANT TEMPERATURE

EUTECTOID STEEL

PHOTOMICROGRAPHS X2500

388
41

BHN 415
RC 44

700

600

500

400

300

200

100

TRANSFORMATION TEMPERATURE °F

TRANSFORMATION BEGINS

650°F

150°F

BHN 682
RC 66

1

10

100

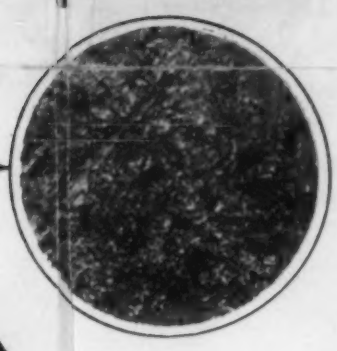
1000

0.5 1 SECOND

1 MINUTE

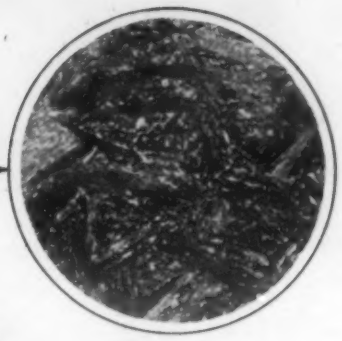
TIME ON LOG

UNITED STATES
RESEARCH



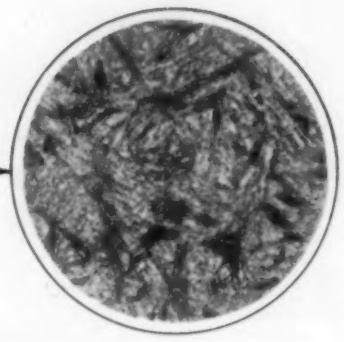
BHN 495
RC 50

550°F



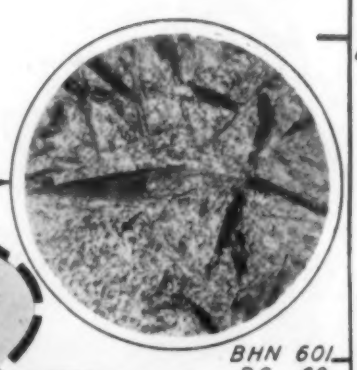
BHN 555
RC 56

450°F



BHN 578
RC 58

350°F

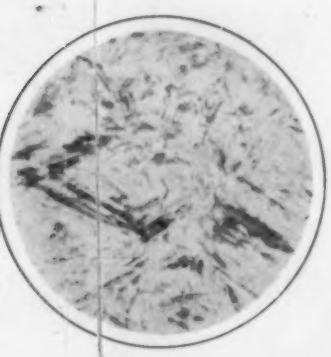


BHN 601
RC 60

250°F

TRANSFORMATION ENDS

BHN 627
RC 64



BHN 653
RC 65

TRANSFORMATION TEMPERATURE °C

300

200

100

0

SECONDS

000

10000

100000

1000000

1 HOUR

1 DAY

1 WEEK

1 MONTH

LOGARITHMIC SCALE

STATES STEEL CORPORATION
RESEARCH LABORATORY
1935

UNIV. OF MICH.

bringing about transformation to a softer pearlite product; stated in another way, the alloy steel hardens more deeply—that is, it can, at a given cooling rate, be hardened through a heavier cross section than is feasible with a carbon steel. Similar remarks apply to the influence of its austenitic grain size upon the hardenability of a steel.

Experimental Procedure

The general procedure used to secure the data embodied in the diagram follows:

> A small specimen of the steel, rendered completely austenitic, is plunged rapidly into a liquid bath of high heat abstracting power (a lead or lead alloy or salt bath), maintained at one of the constant temperature levels, held there for a definite period to permit the transformation to progress, and then immediately quenched in cold water or brine to fix for subsequent observation the condition of the steel at that instant. The specimen must be small enough, and the transfer from the high temperature rapid enough, to ensure that the specimen reaches the temperature level of transformation *while still completely austenitic*; if during this cooling transformation does set in, the purpose is defeated. The length of time each specimen is held in the liquid bath is chosen so as to provide a series of specimens covering the range from untransformed to completely transformed. The austenite still untransformed is by the quench immediately converted to martensite; that which has transformed therefore appears as a darker etching constituent against a lighter martensitic background, and appropriate microscopic technique enables one to estimate the extent of transformation in each specimen. From these observations, made at a series of temperature levels of the liquid bath, curves showing the progress of transformation with elapsed time at each temperature level are drawn, and these, in turn, are summarized in the S-shaped curve. The progress of the transformation may also be followed directly by use of an appropriate dilatometer, or of a solenoid to estimate the amount of magnetic iron formed; the results are in accord with those derived from observation of the series of quenched specimens under the microscope.

Conclusion

The phenomena summarized on the time-temperature diagram of the type illustrated are of fundamental significance to the whole subject of the heat treatment of steels, whether plain carbon or ordinary alloy steels. The general form of the curve is the same for all steels yet investigated in this way, but there are significant differences in the position of the curve on the time scale and minor differences on the temperature scale. The ordinary alloying elements all retard the transformation process under comparable conditions, manganese being especially effective; indeed this retardation appears to be the principal way through which an alloying element affects the mechanical properties of a steel. A thorough understanding of the influence of temperature and time upon the transformation phenomena is thus of great practical importance; and this type of diagram serves greatly to clarify the interpretation and correlation of data relating to the heat treatment characteristics of steels, for it enables us to disentangle the effects of temperature and time in the complex results of different and variable cooling rates on the structure and properties of the finished steel in pieces of different and variable cross-section.

The investigations, the results of which are summarized in this diagram for a single steel, are the work of many members of the laboratory staff, extending over a period of years; further details and discussion may be found in the papers listed below. The large diagram was prepared by J. G. Zimmerman; the micrographs are the work of J. R. Vilella; and the photographic reproduction is due to G. E. Guellich.

Related Publications

"Transformation of Austenite at Constant Subcritical Temperatures," E. S. Davenport and E. C. Bain. *Transactions*, A.I.M.M.E., Iron and Steel Div., Vol. 90, 1930, pages 117-154.

"On the Rates of Reactions in Solid Steel." E. C. Bain. *Transactions*, A.I.M.M.E., Vol. 100, 1932, pages 13-46.

"Factors Affecting the Inherent Hardenability of Steel." E. C. Bain. *Transactions*, A.S.S.T., Vol. 20, 1932, pages 385-428.

"Microscopic Cracks in Hardened Steel, Their Effects and Elimination." E. S. Davenport, E. L. Roff and E. C. Bain. *Transactions*, A.S.M., Vol. 22, 1934, pages 289-310.

"General Relations Between Grain-size and Hardenability and the Normality of Steels." E. S. Davenport and E. C. Bain. *Transactions*, A.S.M., Vol. 22, 1934, pages 879-921.

"Some Characteristics Common to Carbon and Alloy Steels." E. C. Bain. *Yearbook*, American Iron and Steel Institute, 1934, pages 86-119.

"Linear Thermal Expansion and Transformation Phenomena of Some Low-Carbon Iron-Chromium Alloys." J. B. Austin and R. H. H. Pierce, Jr. *Tech. Pub. No. 589*, A.I.M.M.E.

"Dependence of Rate of Transformation of Austenite on Temperature." J. B. Austin. *Tech. Pub. No. 590*, A.I.M.M.E.

"Some Effects of Small Additions of Vanadium to Eutectoid Steel." J. G. Zimmerman, R. H. Aborn and E. C. Bain. Presented at A.S.M. Convention in Cleveland, Oct., 1936.

WHAT HASN'T BEEN ACCOMPLISHED IN 1936

(Continued from page 2)

Some Real Progress

It is a fact that some real progress has been made in many lines in 1936, better stuff is being made and less hooey about either old or new stuff can be gotten away with, but even so, January is no time to sit back with folded hands and smug complacency to contemplate what a swell job we metallurgists as a class did last year. There are lots of unsolved problems, many of them truly pressing, and instead of the job of solving them having come to any sort of a stopping place, or our knowledge being complete, it would seem that 1936 has made even more clear that what we know and utilize is but the tiniest fraction of what we ought to find out and utilize.

In 1946 and 1956 won't the comments on the remarkable advances of 1936 be rather amusing to read? Much that we now think is true and important won't be so then, and many problems now unsuspected, will be the center of interest. So perhaps we might well do a bit of thinking about the problems we didn't solve or didn't even tackle in 1936.

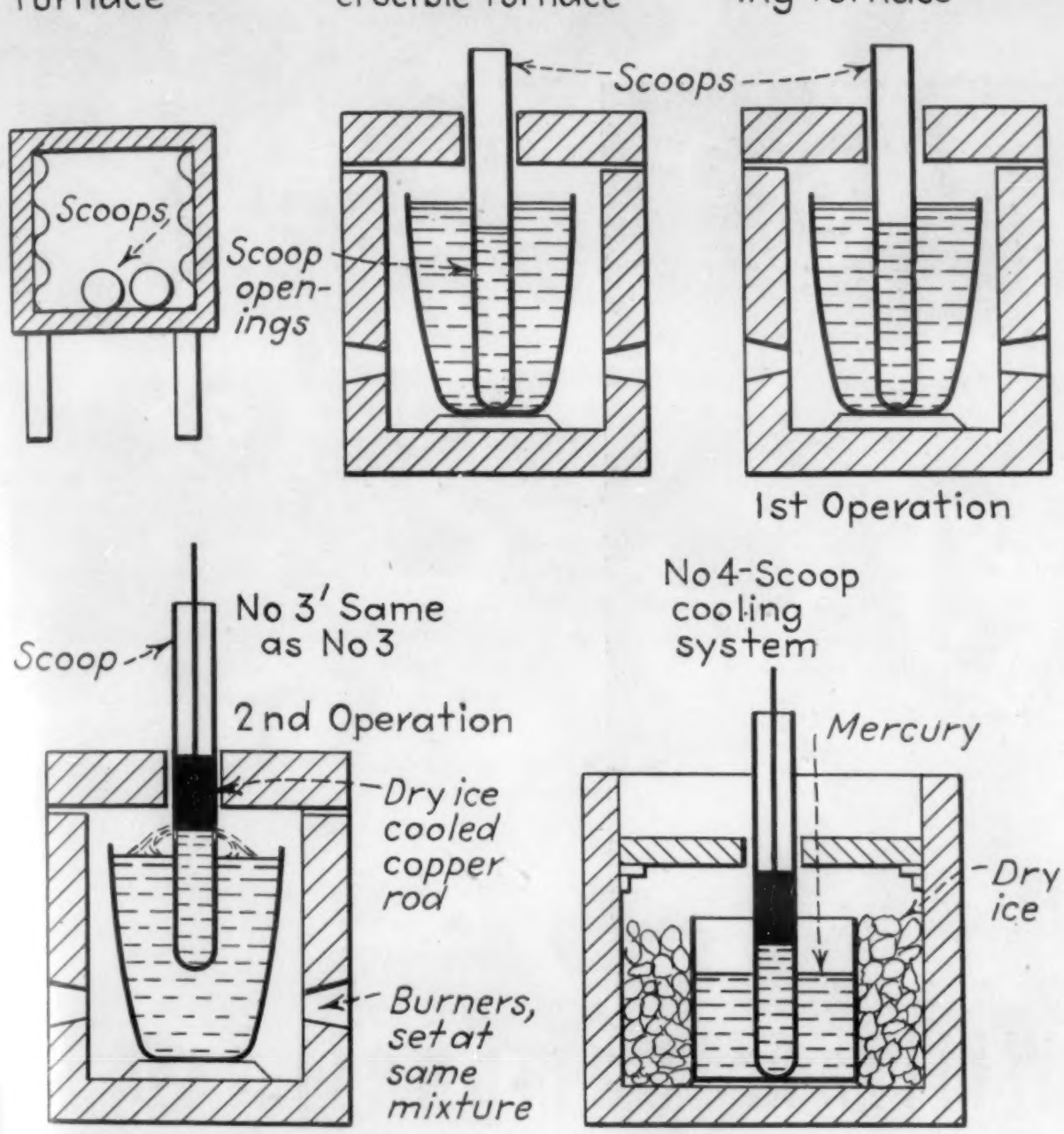


Fig. 1. The Sequence of the Various Operations.

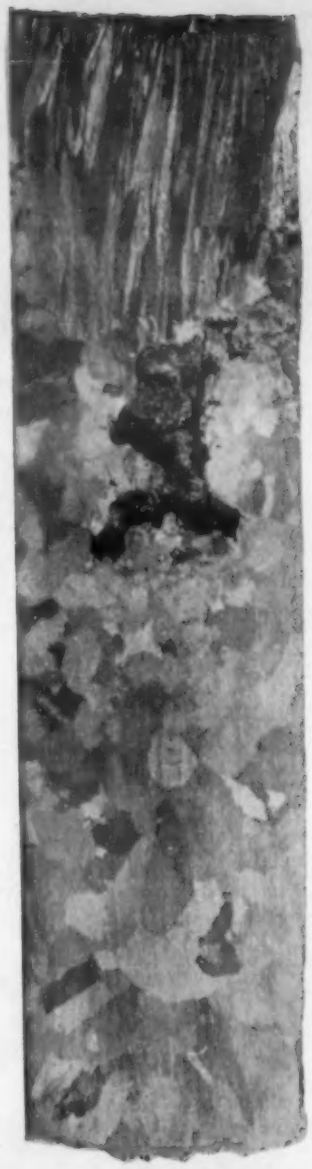


Fig. 2. Etched Cross Section, Full Size, of a Scoop Sample Taken As Described.

SCOOP SAMPLING OF MOLTEN BRASS

In connection with the method of scoop sampling of molten brass and bronze described in our article on pages 261 and 262 of the October, 1936, issue of METALS AND ALLOYS, some details of a modification we are now using, may be of interest.

These modifications are introduced to avoid chilling the melt to be sampled by the introduction of a cold scoop, and to force the cooling of the sample so as to give the least possible chance for escape of gas from the melt prior to solidification.

In our present practice, the carborundum scoop is first preheated in an electric resistor furnace run 150 degrees F. below the temperature at which the metal is to be sampled. Two pots of the metal to be studied are melted at the time in two similar gas-fired furnaces run as nearly alike as possible. One of these serves merely as a further preheater and a wash for the tube, which is immersed in the melt some 15 min. prior to the actual sampling.

When the sample is to be taken, the scoop, now preheated to the full temperature of the melt, is taken from the preheating pot, dumped and at once plunged into the test pot. This insures the scoop being very close to the desired temperature and guards against chilling of the test melt.

The scoop is then raised so that the excess metal runs out of the side hole and a copper plug, previously chilled by dry ice is lowered on to the surface of the metal in the scoop. The scoop is then withdrawn and plunged into mercury, cooled almost to its freezing point by dry ice.

The chilling of the top surface and the chilling of the whole in the cold mercury which immediately follows hinders the escape of gas and inclusions, and also causes the shrinkage cavity to be mostly internal. The size and shape of the shrink cavity and the appearance of the alloy in its fractured segments may then be studied. No attempt is made to save the scoop as the rough chilling treatment weakens its strength somewhat. Fig. 1 shows the sequence of operations. Fig 2 shows the etched cross section, full size, of a scoop sample so taken.

L. KROLL, E. A. ANDERSON, and F. E. BALL,
Dallas Division, Revere Copper & Brass, Inc.

Dr. William Campbell

Howe Professor of Metallurgy at Columbia University, died on the morning of December 16, 1936, at the age of sixty. That his health was uncertain during the past ten years was known to his many former students and his wide circle of friends; nevertheless, they will all be profoundly shocked at his sudden death.

Professor Campbell's many honors and distinctions have been listed in appropriate places, "American Men of Science," "Who's Who in America," etc., and need not be repeated here.

A brilliant student under Sir Roberts-Austen and H. M. Howe, and an able successor to the latter at the Columbia School of Mines, he exerted a profound influence on the development of physical metallurgy in this country since the turn of the century.

As an inspiring teacher he will be remembered by many hundreds of students. As a research worker his list of publications is long. As a practical and practising metallurgist his directive influence was felt in many industries, in the United States Navy in which he held the rank of Commander in the Naval Reserve Force, and in his work, continuous since 1908, as Chairman of the important Committee B-2 on Non-ferrous Metals and Alloys of the A.S.T.M.

It is impressive to realize that in his own lifetime, from student to eminent authority, Professor Campbell saw almost if not quite the whole of the development of scientific metallurgy as we understand the term today, including the development of our fundamental instruments, the thermocouple and optical pyrometers and the microscope. There are but few such men left. Metallurgy thus approaches the end of an epoch. In Professor Campbell's death both the art and the science lose one who played an important part in developing metallurgical tradition. His survivors and successors in the field will, however, prefer to offer a more personal tribute, to say with deepest respect that metallurgy has lost one of its grand old men.

—Edward F. Kern and Eric R. Jette.

A Transparent Mounting

FOR MICROSECTIONS

by E. A. Erdman

Chemical Laboratory, Cutler-Hammer, Inc., Milwaukee, Wis.

A TRANSPARENT MATERIAL which has been developed only recently has been adapted to the mounting of small metallurgical specimens and has proved to be more satisfactory for most purposes than either fusible alloys or bakelite. Originally in the form of powdered resin it becomes, under temperature and pressure, as transparent as glass and is tough, hard, resistant to the action of etching reagents, and adheres excellently to the specimens. It eliminates the differential etching action that frequently takes place when specimens are mounted in a fusible alloy and it also permits examination of the very edge of the specimen. The edges of specimens mounted in soft metal will be rounded off and cannot be examined. This material has, in fact, all of the advantages of a bakelite mounting as well as those added by its transparency.

The hydraulic press used for bakelite mounting can be used with this material. The procedure is similar except that a slightly higher temperature and pressure is required. The transparent mounting is especially useful when an electrolytic etch of a small specimen is desired. It is rather difficult to connect the specimen to the line when only a flat section is available, but with this type of mounting it is easy to mould the connector into the mounting and then remove a portion of it for making the connections to the electric circuit.

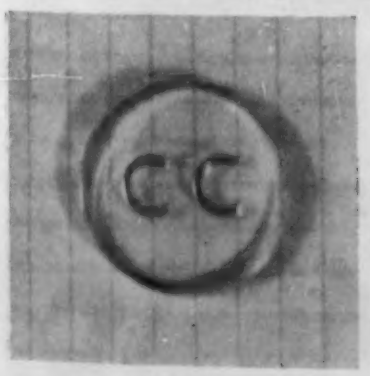
A piece of copper wire is connected to the specimen and the other end is arranged in a flat coil and placed so that it is at the surface of the mounting opposite the specimen. After the mounting is completed, a saw cut is made just under the wire and the coil can then be removed and unwound. Two specimens can be connected in the same mounting almost as easily as one. It is often necessary to locate a certain section under the microscope, such as the cross section of a broken weld. This is facilitated by the transparent mounting because the surface of the piece is visible as well as the cross-section.

When it is necessary to polish and examine a different cross section of the piece under observation, a transparent mounting makes it possible to saw the mounting and specimen exactly as desired because the progress of the saw blade through the mounting can be followed. The fact that the entire specimen is in full view makes identification of the pieces easier than if mounted in an opaque material. Identification numbers can be placed on the specimens themselves.

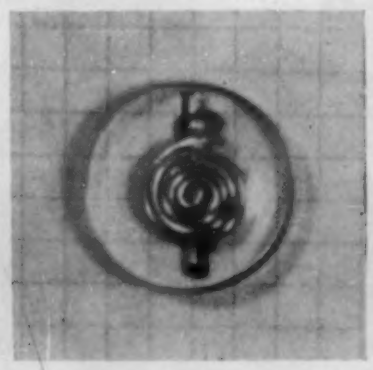
The molding powder is methyl methacrylate and is sold under the trade name of "Pontalite" by the Du-Pont Viscoloid Co. The mounting procedure is similar to that used in mounting specimens in bakelite. The amount of powder used is equal to the desired size of the finished mounting plus a one-third allowance for shrinkage. After the specimens and powder have been put in the mold, it is placed in the press and the resistance heater surrounding the mold is turned on. The pressure is raised to 4000 lbs. per sq. in. and kept at that figure until the temperature has reached 120 degrees C. As the heating progresses the pressure will tend to increase. A small amount of oil must be released from the pressure side of the press, from time to time, to keep from exceeding this pressure. The temperature is then lowered to 85 degrees C, while the mold is still in the press under substantially the same pressure. This is necessary because Pontalite is thermo-plastic. After the mold has reached 85 degrees C., it can be taken out of the press and the mounting removed.

The writer wishes to express his indebtedness to E. A. Giard for originally suggesting this adaptation of Pontalite, and for his helpful advice in developing the mounting technique.

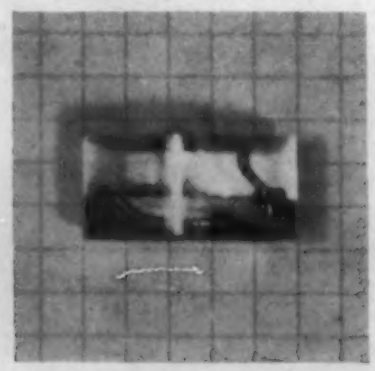
Top View of Transparent Mounting.



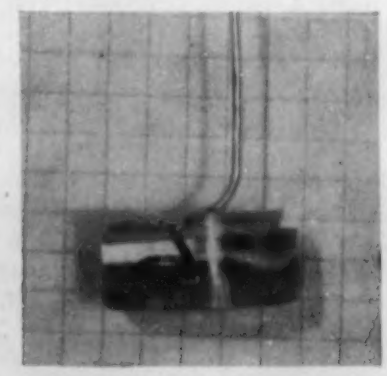
Another Top View of Transparent Mounting.



Side View Showing Specimen at Bottom and Coil of Wire on Top.



Wire Uncoiled and Specimen Ready for Electrolytic Etch.



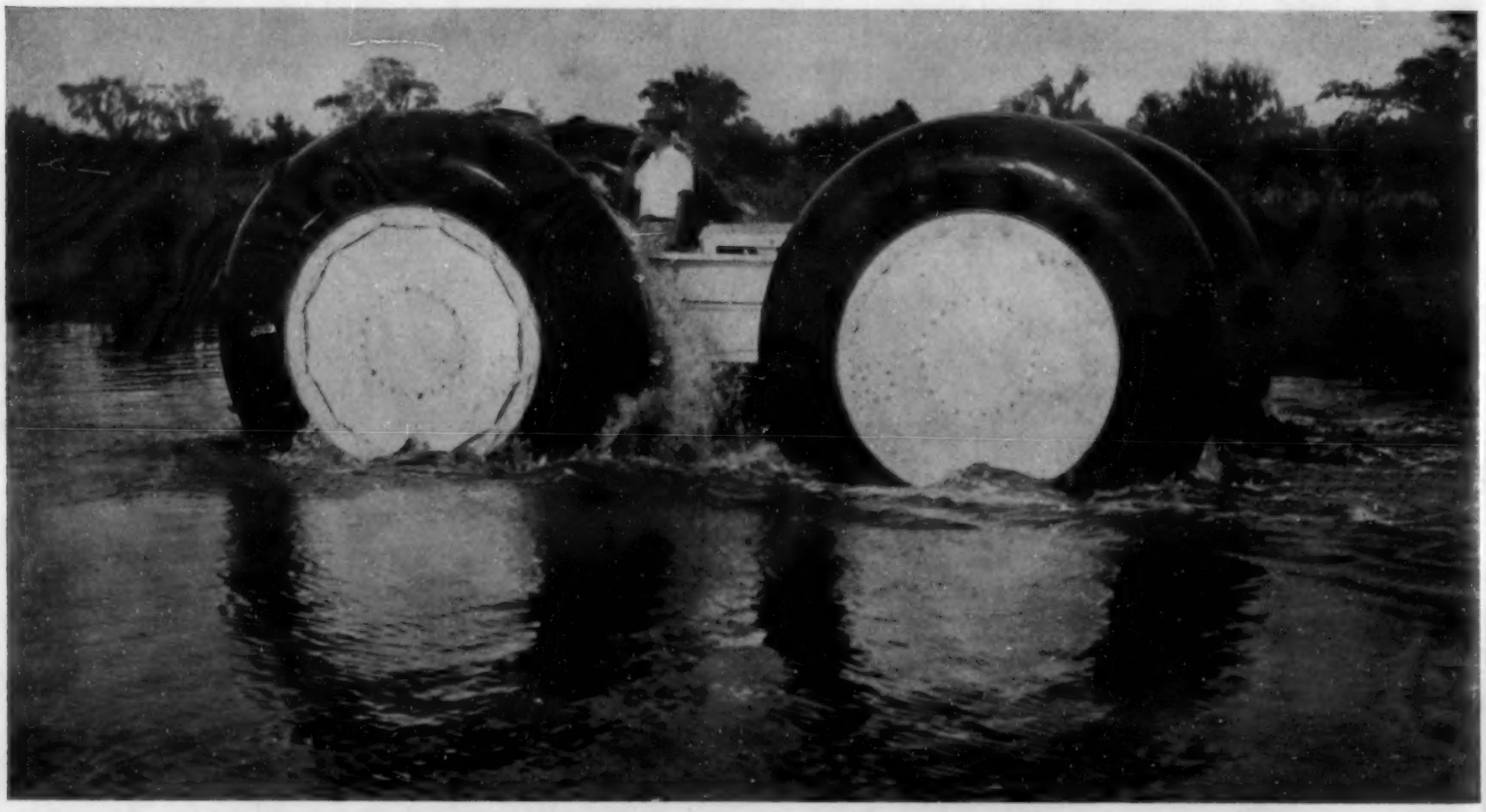
(Continued from page 9)

The next time I saw Dan was at Yokohama in 1929 where I had gone to attend the World Engineering Congress, initiated and sponsored by the Japanese government. Dan and some other Technology men came to welcome us. We talked of the "suffocation incident" as he called it, of 51 years before. Dan was then managing director of Mitsui & Co. and one of the important men of Japan. A few years later he was murdered by a Japanese militarist, presumably because he stood for peace with the world.

Before working at steel, I had a year as chemist with the Providence Gas Co. which I have never regretted because of the knowledge of gas I gained there. I had one experience there which shook my faith in the universality of the diffusion of gases as laid down in the books. A gas-holder, about full of gas, was held for months without receiving any more gas but was continually delivering a little for consumption, which was of course drawn from the bottom. The gas drawn out steadily deteriorated in quality. Its candle-power fell while its specific gravity increased and its nitrogen and carbon dioxide (CO_2) contents, both inert impurities, rose. Then, after some weeks, or perhaps months, gas from that holder became better. Its illuminating power rose while its specific gravity and percentage of nitrogen and CO_2 fell. Then it dawned upon me that stratification or settling of the gases in that holder had taken place; that the heavier nitrogen and carbonic acid had settled to the bottom to some extent, making the gas there heavier and lowering its candle-power. Then, when the gas so enriched with the heavier ingredients had been drawn out, that remaining showed better quality as described.

At the end of 1879, I left the gas company to engage as chemist for the Nashua Iron & Steel Co. at Nashua, N. H.

(To be Continued)



THE MARSH BUGGY

Described as the "world's most unusual conveyance," the marsh buggy can travel on both land and water. It has a marine license and is more of a boat than an auto. It has been built by the Gulf Research & Development Co. for the Gulf Oil Corp.—a conveyance which can carry geophysicists and surveyors over marsh or terrain not traversible by boat or automobile.

The buggy is 22 ft. 6 in. overall, 11 ft. 8 in. wide, and weighs 7,500 lbs. unloaded. It is designed to carry 1,000 lbs. Saving on weight was accomplished by using aluminum and stainless steel alloys. Of the 7,500 lbs., 3,000 lbs. are aluminum. It receives its buoyancy from its rubber tires, 10 ft. in dia. and 33½ in. across. It is now in successful operation.

Silver Alloys as Brazing Materials

FOR SPUDS IN TANK CONSTRUCTION

by H. A. Folgner

Handy & Harman, New York

A RECENT APPLICATION of the comparatively new low temperature brazing alloys containing silver has produced such remarkable results that the procedure followed in using them is well worth reviewing in detail for its value on other applications where conditions are similar.

It is a well known fact that the mounting of pipe flanges or boiler spuds to which piping is connected is among the most troublesome jobs in tank and boiler construction. In the language of the trade, the term "spud" is used to denote a pipe flange which is mounted in a boiler or tank shell.

Conditions a Spud Must Meet

A pipe flange or spud, free from leaks, must be attached to the boiler or tank shell, and stand up under the pulsating effects of the system and also have sufficient mechanical strength to withstand the extreme strain to which it may be subjected when piping is being made up. Often it is impossible to determine in advance whether or not the above requirements have been met until the boiler is in place and has been tested. Then, because of the position of the boiler spuds, it is very costly and difficult to make repairs.

When it is considered that a range boiler or storage tank has from two to five pipe connections, each requiring a spud or flange, the increase in production costs caused by faulty spuds becomes an important item. To eliminate this costly difficulty, the leading non-ferrous manufacturers of storage tanks and range boilers, in conjunction with a well known manufacturer of silver brazing alloys, have worked out a procedure which is simple and economical in application and gives uniformly reliable results.

Procedure Generally Followed

The general procedure followed is to insert a washer or ring of silver brazing alloy between the spud and the boiler shell and to clamp the entire assembly tightly in a jig as shown in Fig. 2. Heating the spud and the surrounding metal with a torch flame to the proper heat causes the silver brazing alloy to flow evenly, bonding the two metal parts together making a strong, leakproof joint.

Fig. 1. Whitehead Monel Metal Hot Water Storage Tank With Three Silver Brazed Spuds.

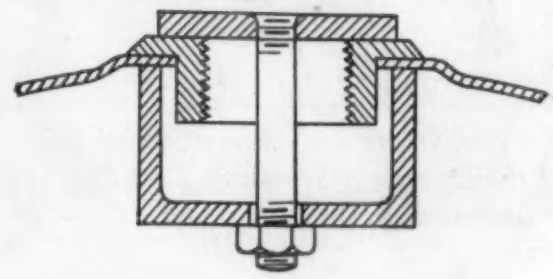


Fig. 2. Simple Jig in Brazing Position.

This method of brazing spuds to boilers, with silver brazing alloys, has been used by some manufacturers for over two years, and it has proven to be most economical and far superior to any other method developed for this type of work.

Existing Brazing Methods Compared

A comparison of existing methods shows why this new procedure is proving so successful. One of the widely used methods of attaching pipe to tanks and boilers is to use a fitting commonly known as a boiler tapping. For mechanical strength, this fitting relies upon a lock nut which is tightened up from the inside of the boiler shell and clamps the boiler tapping and shell together. This joint is then soldered with soft solder. The lock nut and threads are completely covered, some solder flowing between the tapping and boiler shell to make it tight.

This method of mounting works well with galvanized iron tanks but has never been successful on non-ferrous boilers. Under the effect of the pulsation or breathing of the boiler, the soft solder cracks and

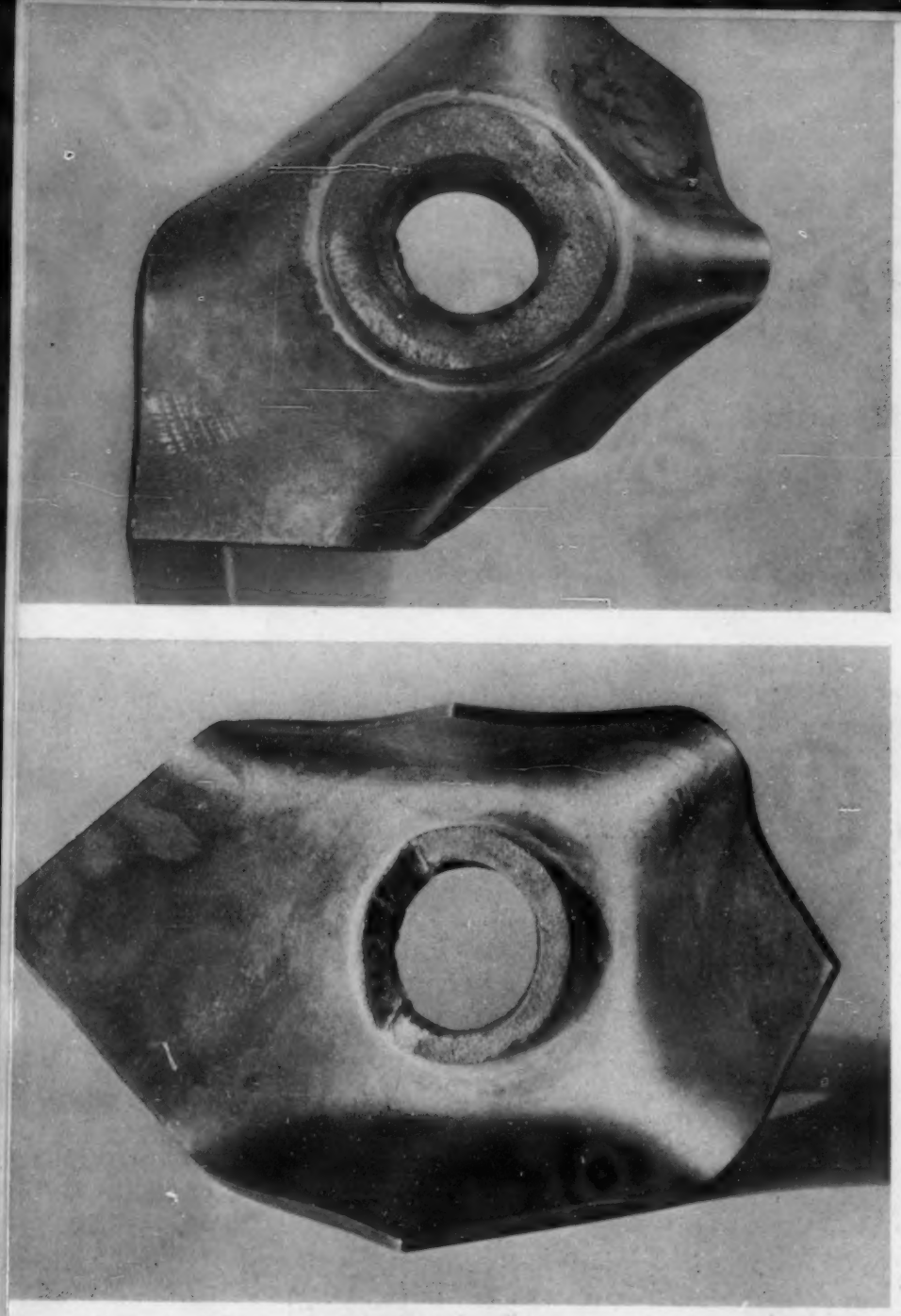


Fig. 3. The Strength of Silver Brazed Joints Can Be Visualized from the Distortion Shown in This Test Specimen. The spud itself was hammered and bent without a break in the brazed joint.

causes leaks. With galvanized iron, there is always the possibility that these cracks will rust tight in a very short time. However, with non-ferrous boilers this is not the case for, after soft solder cracks around a spud, it must be resoldered. This cannot be done from the inside, but must be repaired on the outer surface of the shell which is very difficult to do. Due to the limited strength of this method, when a joint is being made up, the boiler tapping quite often is loosened by the strain to which it is subjected, thereby causing a leak.

In their efforts to eliminate these difficulties, manufacturers have used hard solders in the form of common spelter. These solders, while they give strong joints, are not ideal. The higher temperatures required for their use are likely to change or damage the metals or alloys which are joined. They are also sometimes brittle and fail under heavy stress and shock.

The fabrication of boilers by welding has increased steadily and there are many types of weldable coppers which are being used. This has proved an economical method of fabricating and has worked satisfactorily except where spuds are to be mounted. It has been impossible to make sure that a welded spud is watertight until the whole tank has been completed and tested and then it is rather difficult to make repairs. Often a second welding results in a brittle joint which is a most undersirable feature. Under the pulsation of the boiler, it has been found that repaired joints crack open quite frequently.

Some manufacturers consider this a most serious objection and place their boilers under a very severe pulsation test to make absolutely certain that the joint is not brittle and, therefore, will not crack in service. The pulsation of a boiler, which occurs every time a faucet is opened or closed in a system, must be carefully considered and every precaution must be taken to prevent destruction of joints. A boiler can be strengthened by re-enforcing rings on the inside but the pulsating effect on the spuds cannot be eliminated, particularly when mounted on the boiler shell.

The use of silver brazing alloys to mount spuds has been tested most thoroughly and the reasons for their superiority over existing methods may be better appreciated by considering the physical properties of these alloys and their method of application. They are remarkably resistant to fatigue from bending, vibration, shock and temperature changes. (see Fig. 3) thereby lending themselves well to the requirements of this work.

Two Types of Silver Brazing Alloys

Two types of silver alloys, one flowing freely at 1300 deg. F. and the other at 1175 deg. F., have been widely adopted for this type of work. The alloy flowing at 1300 deg. F. is patented and intended for brazing non-ferrous metals only. Its composition is:

Copper	80 per cent
Silver	15 per cent
Phosphorus	5 per cent

and its starts to melt at 1185 deg. F., being free flowing at 1300 deg. F. The brazing alloy, flowing at 1175 deg. F., is particularly suited to joining stainless steel, Monel metal, nickel and its alloys, copper, brass, bronze, Everdur or any of the other well known types of weldable copper alloys which are generally used for range boiler construction where fast working at about 1200 deg. F. for brief periods is desirable so as to avoid overheating and excessive grain growth. The composition of this patented alloy is:

Silver	50 per cent
Copper	15½ per cent
Zinc	16½ per cent
Cadmium	18 per cent

and its melting range is 1160 to 1175 deg. F. They provide high strength and ductility and flow freely at temperatures safely below the range likely to injure the metals to be brazed. The high degree of strength obtained in most cases is as high or higher than that of the materials joined. Used with a good flux, having a low fluid temperature which permits taking advantage of the alloy's low melting point, only a small quantity of brazing alloy is needed to make tight fitting joints.

The other brazing alloy flows equally well and strength and ductility are very good. It requires a slightly higher temperature, 1300 deg. F., to braze satisfactorily. The advantage of this particular material is that it is self-fluxing when used on copper. It flows freely into the metal, actually alloying with it, making tight, permanent joints. It can be used only with non-ferrous metals.

Good silver brazing alloys are free-flowing within

their respective temperature ranges and have a remarkably quick penetrative quality, alloying readily with adjacent metal sections to form firm bonds. The photomicrograph shown in Fig. 4 indicates the degree of penetration of the solder into the brazed parts, one of the reasons why the joint is generally stronger than the metal parts it joins.

Economy in Their Use

These alloys are also economical to use. It is a delusion to believe that because the essential alloying element is relatively expensive that the cost of silver brazing is high. The washer of silver brazing alloy placed under a spud is about 0.010 in. thick and its area is equal to that of the flange. Thus it is possible to definitely determine the cost of the brazing alloy. In some instances more than a ½ lb. of 50-50 soft solder is specified per joint in attempting to get soundly mounted spuds. In a case like this, a direct comparison of material costs shows the silver brazing alloys to be more than 50 per cent lower and, in addition, a less expensive type of spud can be used.

Very little of the silver brazing alloy is required regardless of the nature of the joint to be made, in fact so little is generally required to make a joint that the joint is usually inconspicuous. There are no objectionable masses of metal outside of a well made silver brazed joint. For this reason, it is entirely suited to the brazing of boiler spuds to range boilers where appearance plays a very important part.

The Brazing Operation is Simple

Brazing with silver solders is relatively simple. A few easily learned principles carefully followed will always produce good work. It is obvious that all parts that must be brazed should be thoroughly cleaned. All dirt, oil and grease should be removed chemically or mechanically. This insures thorough removal of oxides on the metal surface by the flux.

When pre-heating, it is necessary to protect the surface from oxidation caused by the torch flame. Therefore, it is necessary to use some medium which will absorb the oxides formed while heating and thereby aid the flow of the brazing alloy. As is generally known, the purpose of a flux is to assist the free-flowing action of the brazing alloy and, at the same time, protect the metal to be joined against oxidation as well as to dissolve whatever oxides may be formed during heating. Obviously, therefore, a flux which will liquefy at or below the melting point of the solder and will not readily volatilize is to be desired.

Fluxes and Their Bases

Borax forms the base for many fluxes. It has some advantages and also certain short-comings. A borax and boric acid combination is frequently used but, despite the compensating features of one or the other, their limitations depend upon the degree of fluidity which sets the temperature of usefulness for brazing between 1400 and 1600 deg. F. As the boric acid content increases, the viscosity increases and higher temperatures are necessary to provide sufficient fluidity for satisfactory use. Different salts must, therefore, be employed in order to braze at temperatures considerably under 1400 deg. F. and which is to be preferred in this type of work.

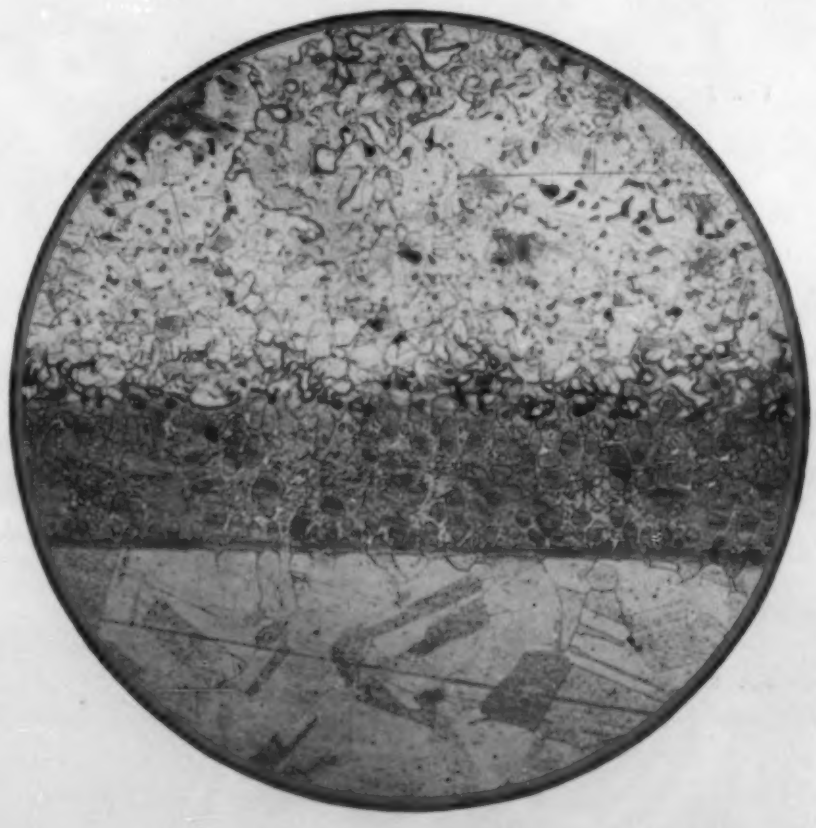
Therefore, those using low temperature brazing alloys need a low temperature flux; the best known of which is a patented flux in paste form having a potassium fluoride base that starts to liquefy at 900 deg. F. and becomes extremely fluid and active at 1200 deg. F. It remains stable to 1600 deg. F. This flux can be readily mixed with water to the desired consistency and applied evenly with a brush over the surface to be brazed. It does not bubble or flow away under the torch and any excess flux coating can be easily softened and washed away with hot water.

How to Apply Fluxes

Correct application of flux calls for covering all parts of the joint and brazing alloy with flux. When used in paste form, the flux should be brushed evenly to cover the surface of the surrounding parts. This protects against further oxidation, absorbs oxides formed during heating, and aids in the flow of the solder.

To obtain sound joints, the brazing alloy must be fully melted. For this purpose, the oxy-acetylene torch is preferred because brazing temperatures can be obtained quickly with a reducing flame and heating can be confined to a small area. Gas from city mains, with oxygen or compressed air, can be used but are slower and spread the heat over a wider area of metal. The torch flame should be played uniformly over the part to be heated to prevent overheating in spots and excessive oxidation. The spud and surrounding metal should be heated slowly with a soft flame. Keeping the flame in motion, and heating uniformly, produces the required temperature over a sufficiently large area without overheating. This is particularly true in working on copper which is a rapid conductor of heat. When heating two different kinds of metals having approximately the same gage or mass, favor the metal that is the more rapid heat conductor.

Fig. 4. The Alloying of Silver Alloys With the Metals They Join is Well Illustrated in This Photo-Micrograph of a Joint Between Bronze and Copper. Magnification, 100 diameters. The upper layer is bronze, the middle portion is silver brazing alloy and the lower layer is copper.



The flame should be played more frequently on the spud which requires more time to heat because of its greater mass. The boiler shell, in most cases, is relatively thin and it is desirable to avoid the tendency to overheat the thin section of metal before getting sufficient heat in the spud.

Precautions in Pre-Heating

In pre-heating, certain precautions should be observed. The operator must judge the correct heating temperature, preparatory to the flowing of the solder and must prevent overheating of the metals being brazed. The low temperature flux recommended is a good heat indicator as it is extremely fluid at 1200 deg. F. and can be readily observed by the operator. He should not face the light and permit it to distort his judgment. The work also should be shielded from air drafts which cause uneven cooling.

Silver brazing, due to the low heat required and the free flowing qualities of the alloys, is much faster than welding. In pre-heating, a soft neutral flame should be played in a circular motion close to the joint, quickly melting the silver alloy into place. Thus the high heats which are necessary for brazing with base metals and for welding are avoided.

Types of Spuds and Pipe Flanges

Many types and shapes of spud and pipe flanges are used in boiler and tank work. A few of the more generally used types are shown in Figs. 5 to 8. The greatest difference between them is the method by which they are made. Spuds which are made of weldable coppers are usually forged, others are usually cast. However, either type may be brazed successfully and in all cases it is possible to use an insert of silver brazing alloy and to apply pressure in such a manner as to produce the close clearances which are essential for good brazing.

The method of applying pressure to the joint while brazing may be done in various ways. The simplest way is to use a small jig, similar to that shown in Fig. 2. The small screw clamp applies pressure to the flange of the spud and to the surface of the shell. When heat is applied, the various members expand and when the brazing alloy melts, the clearance between the shell and the spud is reduced to a minimum. Providing the necessary equipment is available, it is also possible to apply pressure by means of a pneumatic ram during the heating period. This also produces minimum clearances in the joint.

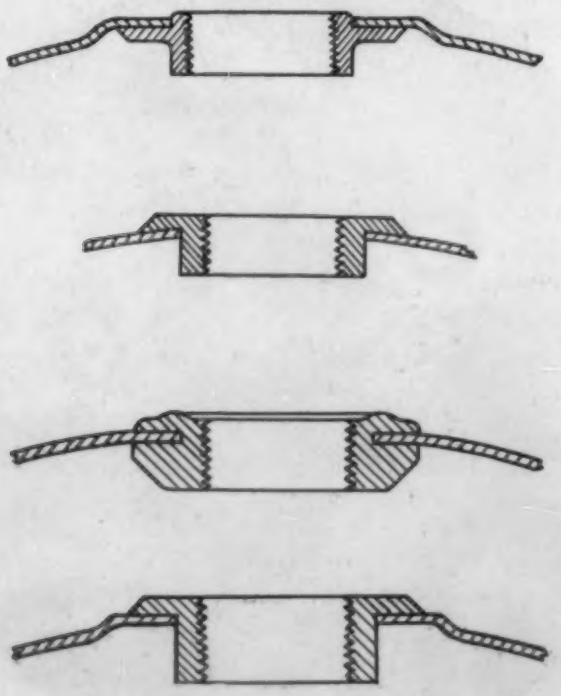


FIG. 5

FIG. 6

FIG. 7

FIG. 8

Methods of Applying Pressure

Caution should be taken in applying pressure. The points of application should be located at the thickest sections of metal. The members of the jig should be located so as to prevent any bending or distortion of the boiler shell during the brazing operations. It must be borne in mind that at elevated temperatures the strength of the material is momentarily reduced.

The various types of spuds shown have been adopted by the manufacturers for various reasons. Fig. 5 shows a type used in Monel metal tanks which gives a very neat appearance, only the narrow rim of the spud being visible from the outside. Fig. 6 is a radius type or curved spud commonly used in the low priced field. It eliminates the necessity of embossing the boiler shell as the curvature of the spud readily fits the curved surface of the shell. However, it cannot be used in the headers of range boilers.

Fig. 7 shows the clinch type assembled. This type of spud was designed to be turned over or peened under pressure, to obtain mechanical strength. The manufacturer formerly welded these spuds but now uses a silver brazing alloy and still retains the peening feature. This was done for the sake of appearance as with this type of spud it is possible to obtain a rather inconspicuous flange on the surface of the boiler. Simultaneously it also produced a flat surface in the boiler shell and eliminated the necessity for applying pressure during the brazing operation. The washer of silver brazing alloy was inserted between the larger flange of the spud and the boiler shell and the entire assembly clamped together during the peening operation. When heat was applied the silver brazing alloy flowed completely around the joint and between the outside flange and the shell, producing a very excellent brazed spud.

Fig. 8 is a type of spud quite similar to the one in Fig. 6 except that it has a straight flange. It is quite similar to the commonly used boiler tapping but represents the transition of this type of spud to a type more suitable to the brazing methods as described in this article. It eliminates the threads required on the outside of the spud for the lock nut, thereby being considerably cheaper. It can be seen from these illustrations that any type of spud can readily be brazed without difficulty.

While the brazing procedure outlined has dealt entirely with spuds for storage tanks and range boilers, the same general procedure may be applied to many similar problems, whenever it is necessary to join fittings to thin sections of metal and produce strong and leakproof joints which will give long service at low production costs.

The use of silver brazing alloys for work of this nature may be new to many but their growing use is the result of long study and research both in their development and in their application in the industrial field.

THE MANUFACTURE OF

Oxygen-Free High-Conductivity Copper

by Edwin F. Cone

Charging Cathodes of Electrolytic Copper into the Side of the Reverberatory Furnace.

ONE OF THE INTERESTING and striking facts of metallurgy is that the presence of very small percentages of certain elements in a product often deleteriously affects its properties. Conversely the addition of small quantities of an element in a definite product often bestows desirable properties, sometimes attainable in no other way. The problem, however, of removing the apparently poisonous element is many times a difficult one.

This is particularly true of copper. It has been known for years that small percentages of oxygen in practically pure copper have harmful effects—percentages down to 0.03 to 0.05 oxygen. It has also been recognized that, if oxygen-free copper of high electrical conductivity could be commercially made, decided advantages would result. Small percentages of oxygen in copper are present as cuprous oxide—Cu_2O—which precipitates at the grain boundaries and adversely affects the properties. By far the greatest proportion of the production of the refineries is tough-pitch copper which normally contains 0.03 to 0.05 per cent oxygen or 0.27 to 0.45 per cent cuprous oxide. Copper free from this small amount of oxygen has definitely superior fabricating properties because of its extreme plasticity or ability to withstand severe cold working without fracture.

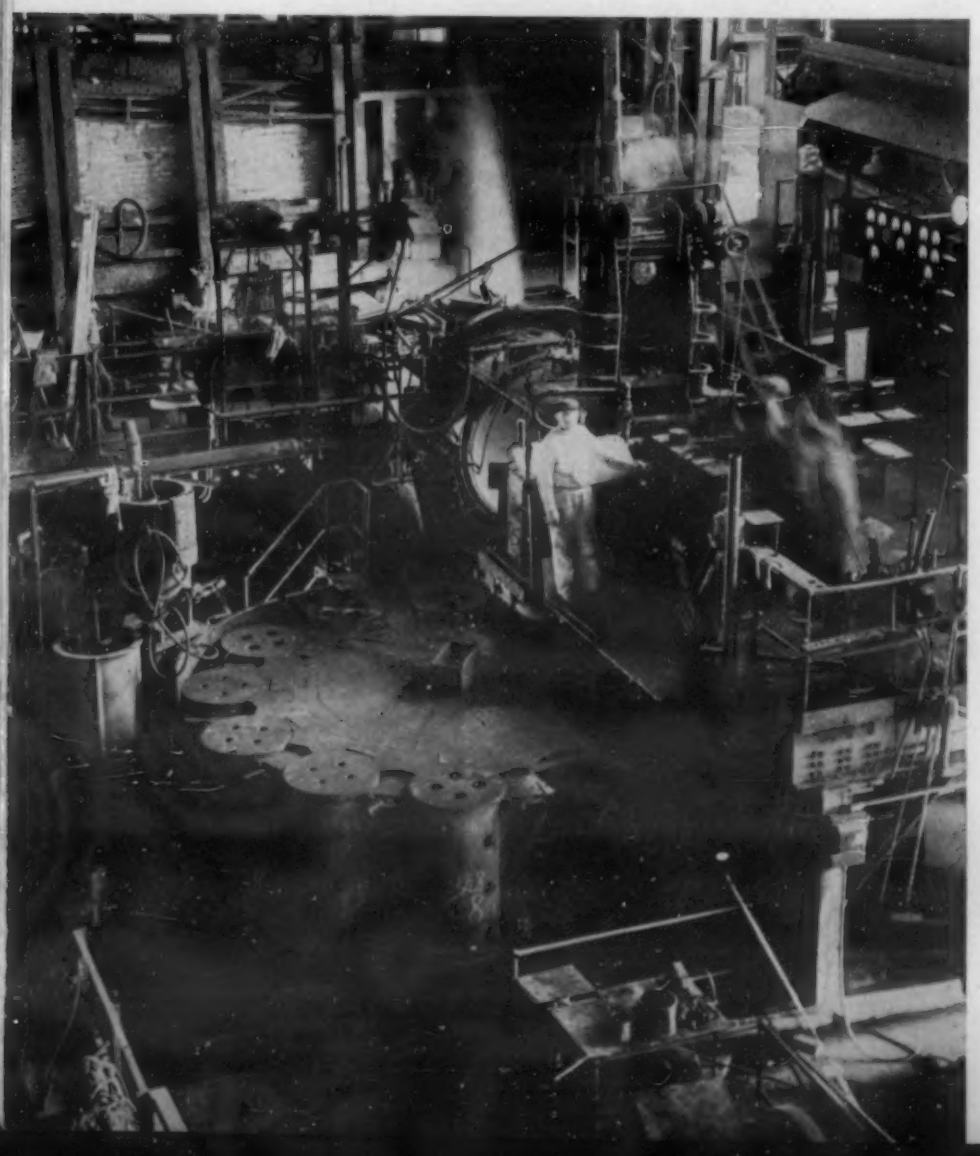
Usual Methods of Deoxidizing Copper

The problem of deoxidizing copper is not difficult metallurgically if the maintenance of its electrical conductivity may be ignored. However, over 50 per cent of the total production of the metal is consumed in the electrical industry. Consequently, if a deoxidizing treatment results in decreased conductivity, the usefulness of the product is inherently limited to a relatively small field. For example, copper deoxidized with phosphorus has been produced for years. Its enhanced ductility and toughness have resulted in the virtual exclusion of tough-pitch copper for the manufacture of pipe and tubing. But ordinarily to insure its freedom from cuprous oxide, enough phosphorus is introduced into the molten oxygen-bearing copper, taken from a reverberatory furnace, to react with all the oxygen present and leave in the finished product an excess of from 0.015 to 0.025 per cent phosphorus. Owing to this residue of deoxidizing agent, phosphorized copper usually has a conductivity of only 85 to 88 per cent, compared to 100 to 101.5 per cent for tough-pitch copper, which renders the former unfit for most electrical purposes.

One or two producers do quite regularly make phosphorized copper with only the smallest excess of phosphorus

Molten Copper Flowing Continuously from the Reverberatory Furnace through a Covered Trough into the Deoxidizing Unit.

The Large Rotary Table Carrying the Molds is in the Center Foreground. At the right foreground can be seen the pour hearth. In the background is the reverberatory furnace.



and correspondingly better conductivity than the usual figures, but they find it an extremely ticklish operation to secure this exact balance.

Experiments by many investigators have been carried out in an effort to produce deoxidized copper acceptable to the electrical industry. A variety of agents such as calcium, lithium, silicon, manganese, calcium boride, and others have been found effective and some have even been used commercially, although only on a small scale for special purposes. In the first place, some of these agents are almost prohibitively expensive and what is more important, the results have not been consistently successful because all tend to have a harmful effect if too much remains in the product, and their use apparently has not been susceptible to adequately precise control.

A New Method Described

Today there is in large commercial operation a new method and apparatus, patented in the United States and foreign countries, for making oxygen-free copper that is also free from residues of deoxidizing agents and has a conductivity equal to that of tough-pitch copper. After several years of extensive experimentation and research, the United States Metals Refining Co., at its plant at Carteret, N. J., has developed and patented several processes for the production of oxygen-free copper. One of these is now being used to produce this grade of copper, which is known as "OFHC." It is the object of this article to describe this process for the first time.

The most novel characteristics of the OFHC process are that it is continuous and that it depends upon the combined use of charcoal and a controlled atmosphere for its metallurgical results. The charcoal is employed as the deoxidizing agent; the atmosphere or gas prevents exposure to the air and consequent contamination with oxygen.

A Reverberatory Furnace

Cathode copper, which is oxygen-free, is charged into an oil-fired reverberatory furnace, conventional in construction, but unique in operation, since the usual intermittent cycle has been eliminated. One of the illustrations shows the charging operation at the side of the furnace. Since the process is continuous, precisely as much copper is charged as is taken out, that is, the charging is balanced by the rate of pouring. The continuously molten bath of about 75 tons of metal is poled at intervals with a large green wood pole from the end opposite the firing end of the furnace so as to maintain a constant oxygen content at about the tough-pitch point. Samples are frequently taken for microscopic examination to determine the oxygen content, which is regulated within the limits, 0.03 to 0.05 per cent.

The Deoxidizing Unit

From the reverberatory furnace the metal flows in a constant stream, at a temperature of 1150 deg. C. or 2100 deg. F., into a refractory lined trough which conducts it under a cover of charcoal, into the second unit of the process where it is deoxidized.

The deoxidizing unit is a specially-constructed piece of apparatus, refractory lined and filled with high-grade wood charcoal. The metal passes through the charcoal by gravity, as a falling stream. By its intimate contact with the charcoal, the oxygen (0.03 to 0.05%) is removed. The reactions which are believed to take place in this unit are:

$$C + Cu_2O = 2Cu + CO$$
$$CO + Cu_2O = 2Cu + CO_2$$
$$C + CO_2 = 2CO$$

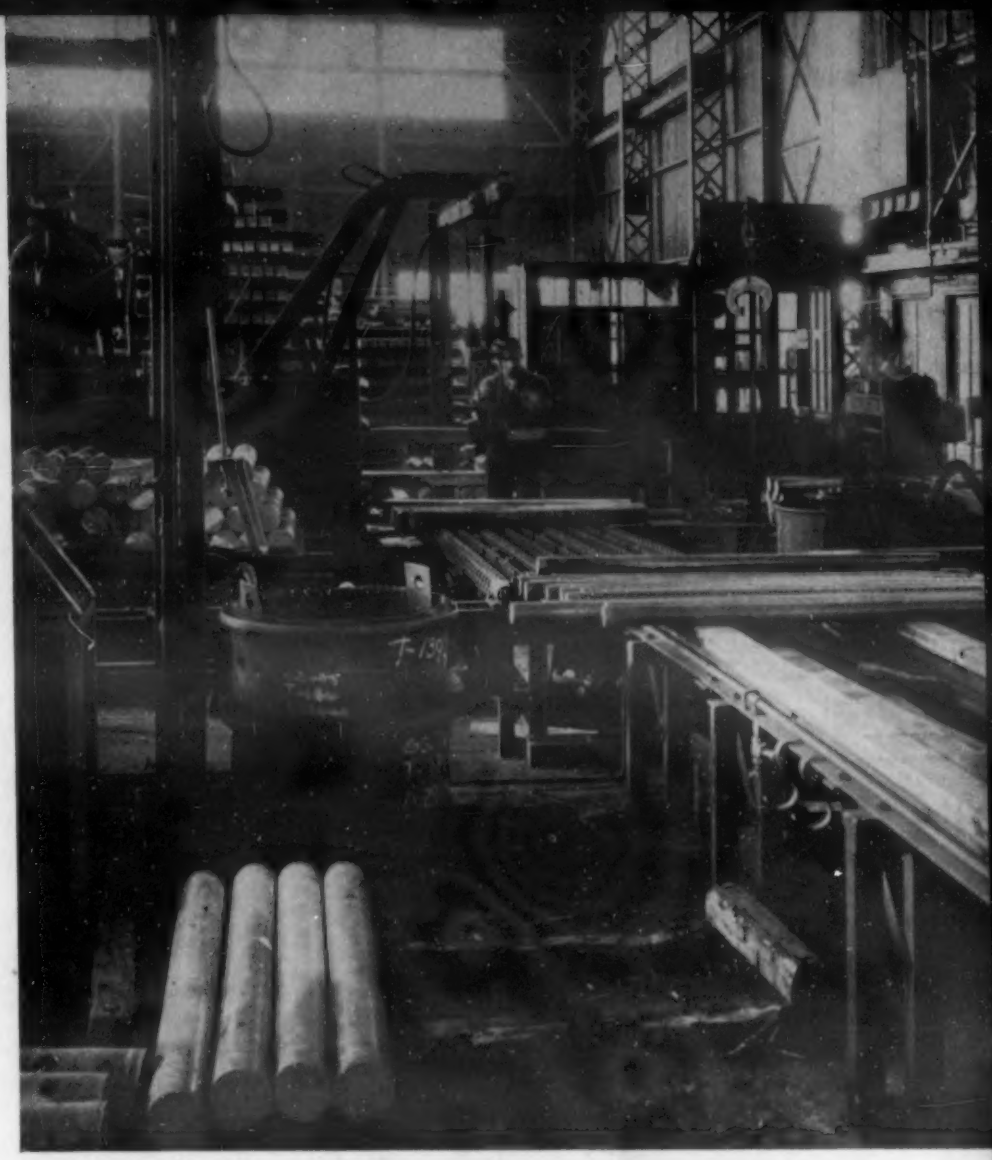
That is, the charcoal acts on the cuprous oxide to form copper and carbon monoxide which also reduces the cuprous oxide to copper and forms carbon dioxide, which in turn is reduced by the charcoal to carbon monoxide. One of the illustrations shows the hot metal flowing from the reverberatory furnace into the trough and then into the deoxidizing unit. The only brief interruption of this stream is occasioned by the infrequent but necessary replenishment of charcoal as it is consumed.

Controlled Atmosphere Introduced

From the deoxidizing unit the metal, now free from oxygen, passes through a specially-designed spout and into an enclosed trough or launder. A controlled atmosphere is maintained around the spout and stream of metal and in the enclosed trough. This is charcoal producer gas containing about 27 to 28 per cent CO, 0.50 per cent CO_2, with the balance nitrogen. The gas is preferably free from hydrogen, hydrocarbons, and water vapor as well as possible oxidizing components.

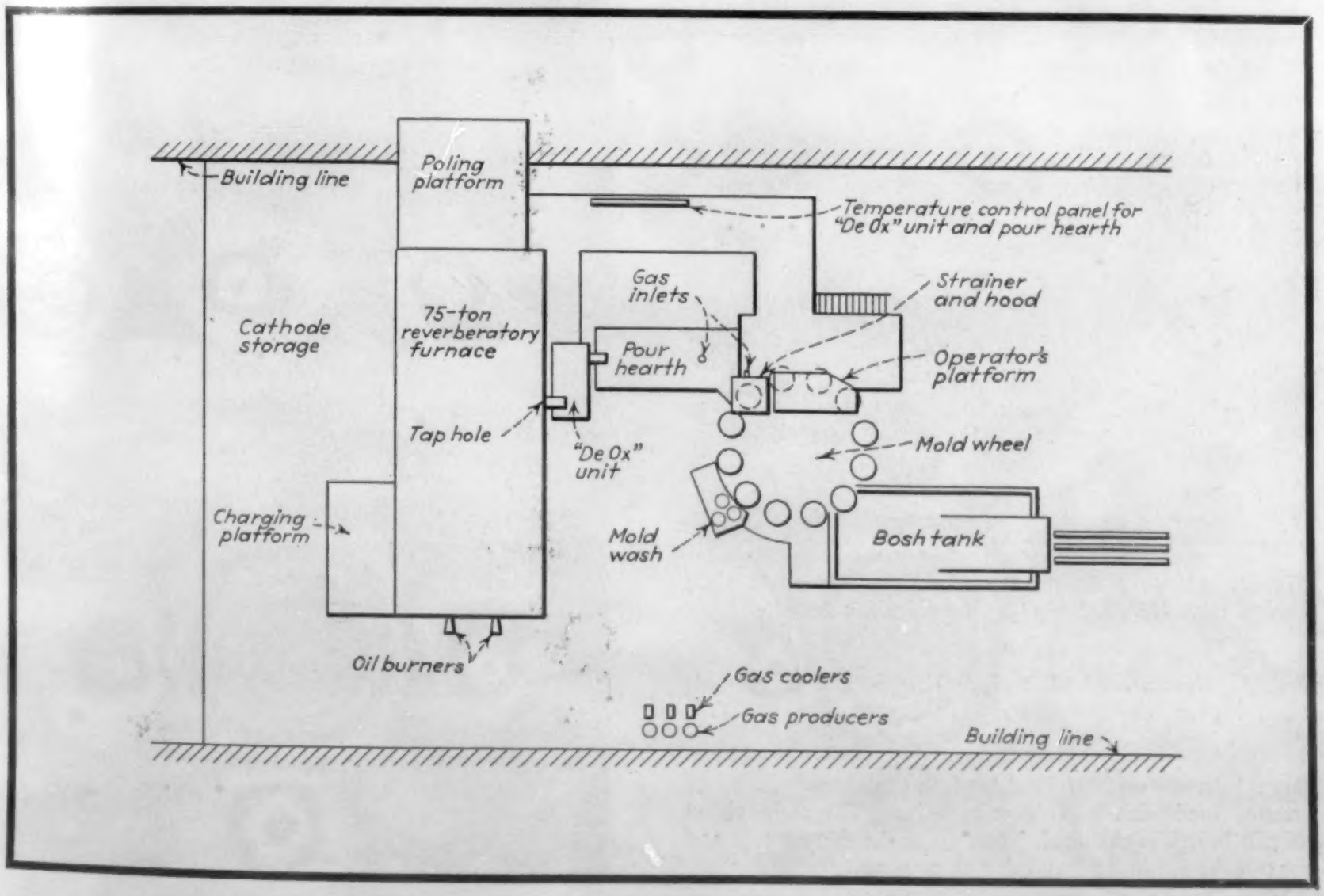
The Pouring Hearth

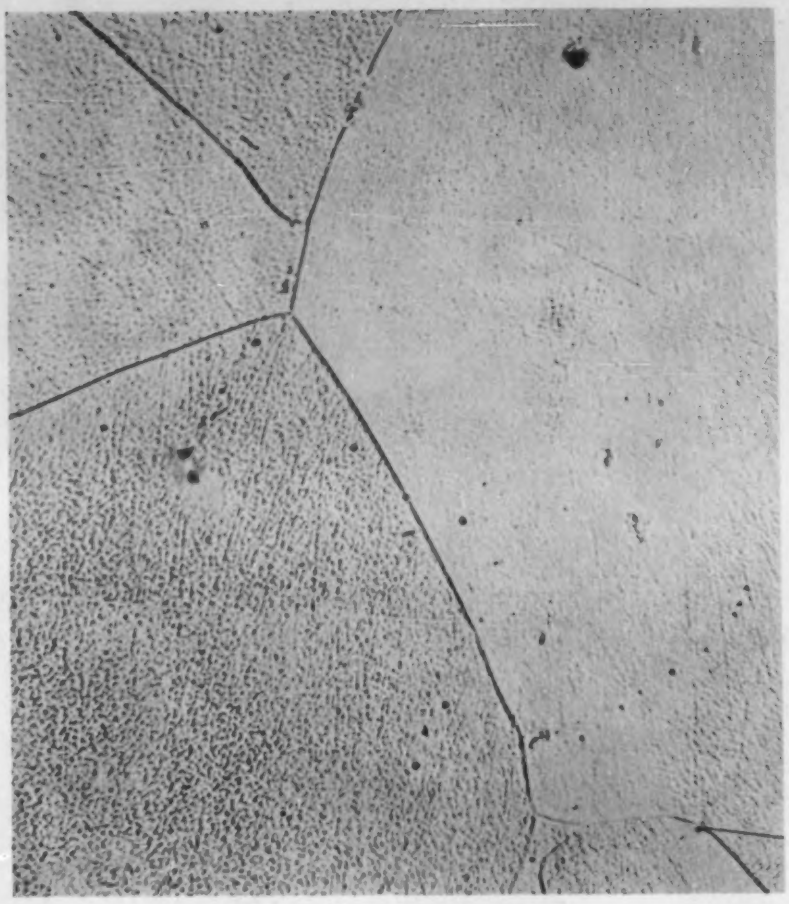
Previous to casting the oxygen-free copper into billets, cakes and wire bars, it passes from the trough or launder just mentioned into a pouring hearth of special design in the form of an elongated cylindrical hearth in which a



One End of the Inspection Rack with Piles of Various Shapes in the Background.

General Layout of the Various Components of the Plant.





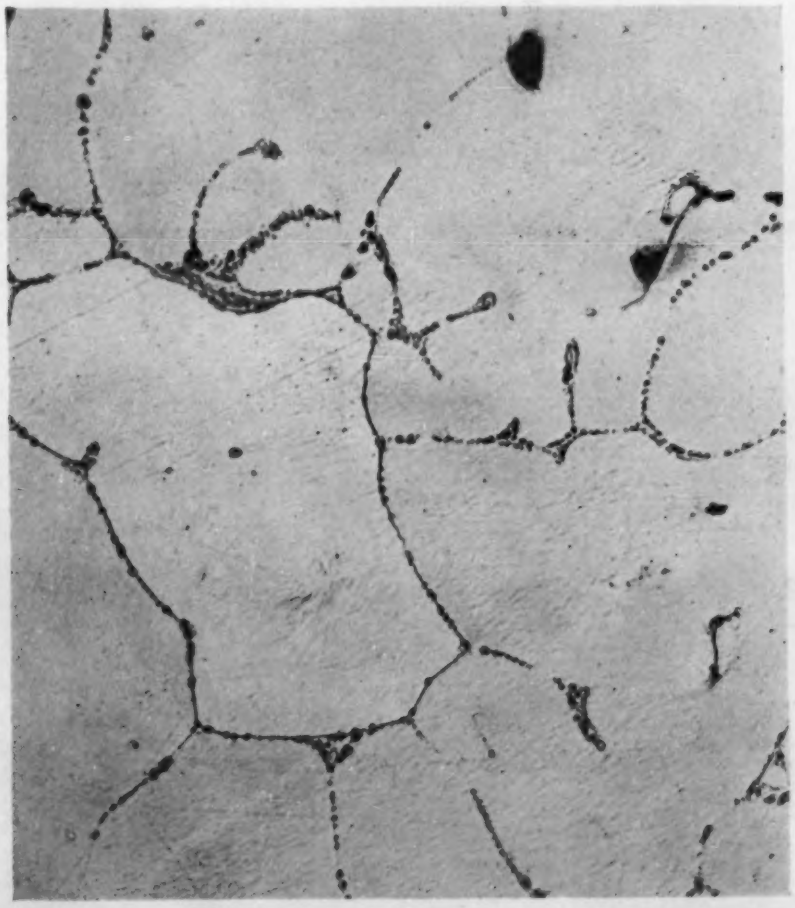


Fig. 1. (Upper) Structure of OFHC Copper As Cast. Etched with NH_4OH H_2O_2. Magnification 200 X.

Fig. 2. Structure of Electrolytic Tough-Pitch Copper As Cast. Etched with NH_4OH H_2O_2 Magnification 200 X.

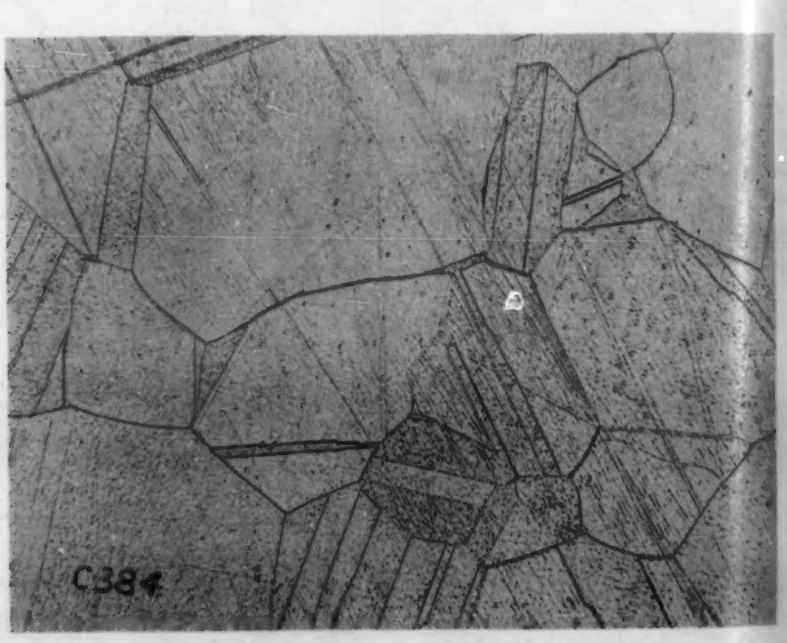
large bath of metal is constantly maintained. It is, of course, lined with suitable refractories. The main object of this hearth is two-fold: To regulate the temperature and control the stream of metal during pouring.

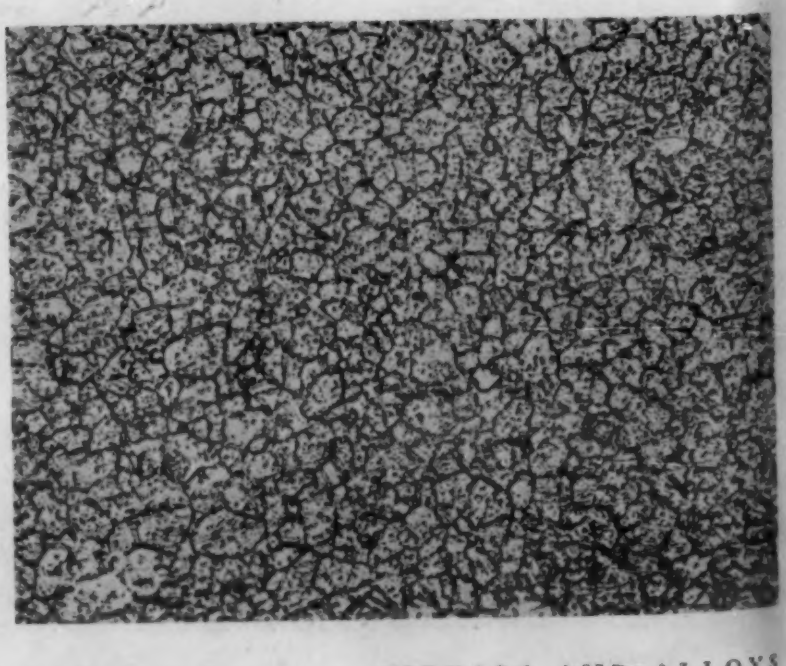
Here again charcoal is present, the entire bath being covered with it. The chamber also is filled with the charcoal producer gas. The flow from the deoxidizing unit is regulated (back at the reverberatory furnace) to suit the pouring rate. Gas seals are provided at both the receiving and discharging ends of the pouring hearth and are maintained unbroken through any angle of tilt for pouring. At diagonally opposite ends of the hearth, there are heating units of the low frequency induction type which serve to regulate the temperature of the metal before it is poured. Aside from the fact that molten oxygen-free copper has been maintained in this unit uninterruptedly since it was first put into service a number of years ago, probably the most unique feature of its operation is that the temperature is controlled automatically within plus or minus 10 deg. C. by refractory encased thermocouples immersed in the bath.

Structures (Below) of Hard Drawn 12 Gage Wire, Heated in H_2 at 850 deg. C for ½ Hr. Etched with ammoniacal ammonium persulphate and repolished, which removes the crystal pattern from the etched surface, revealing the true "lace pattern."

Fig. 3. (Upper) OFHC Copper at 100 X. Nothing visible but the scratches.

Fig. 4. (Lower) Tough-Pitch Copper at 100 X. The open spaces shown in about their true dimensions.

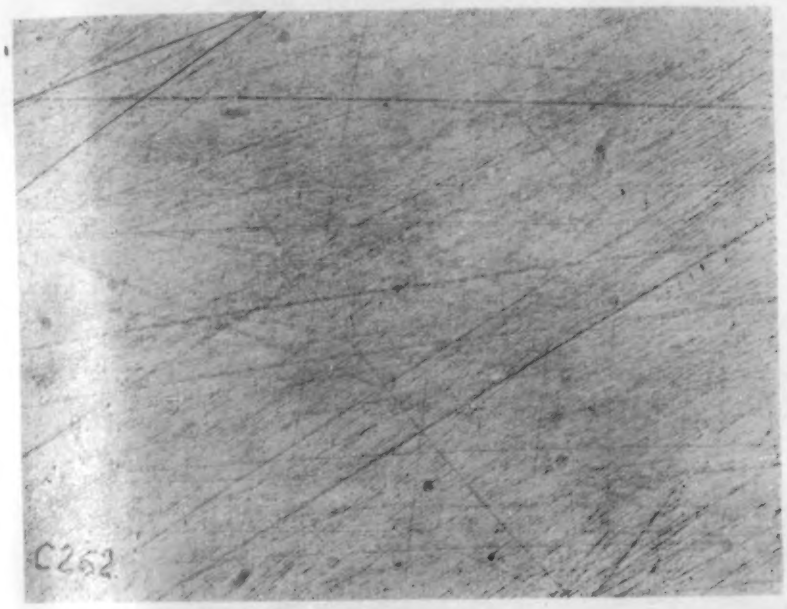


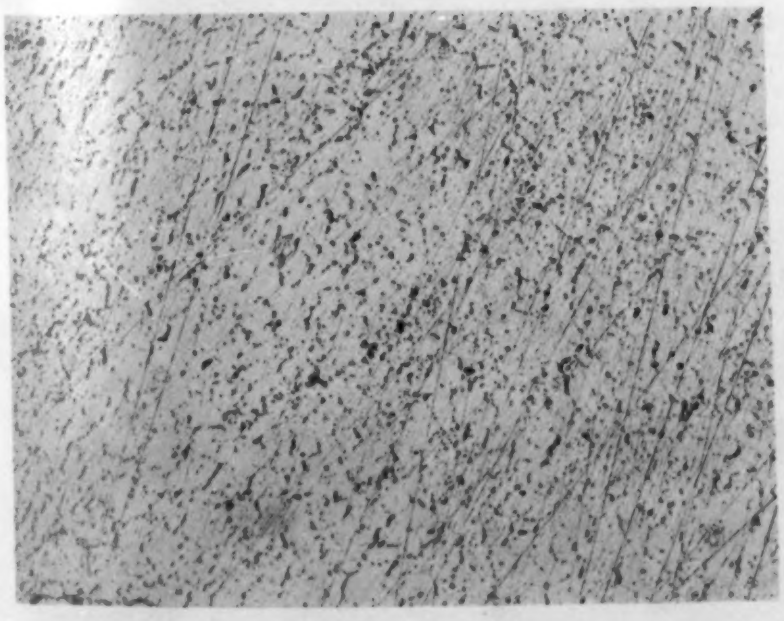


As far as is known automatic temperature regulation for molten copper has never before been employed in a commercial plant.

For pouring the finished copper from the mechanically rockable pouring hearth, the spout is enclosed in a hood which also is filled with the controlled atmosphere, i.e., charcoal producer gas, to surround the stream of metal as it flows from the hearth into the molds and thus completely prevent any reoxidation of the copper. Within the gas-filled hood and below the spout there is an electrically-heated refractory funnel or strainer which directs the stream of metal into the mold cavities.

The various shapes, wire bars, billets and cakes, are poured in water-cooled molds. These are mounted on a rotating platform about 20 ft. in diameter. A plurality of each of these regular refinery shapes is poured simultaeously, and, an important feature, all are cast vertically.





Structures (Above) of Hard Drawn 12 Gage Wire, Heated in H_2 at 850 deg. C for 1/2 Hr. Etched with ammoniacal ammonium persulphate, which unmistakably identifies the "lace pattern" of tough-pitch copper.

Fig. 5. (Upper) OFHC Copper at 100 X. A few etching pits, due to drastic action of the persulphate, can be seen.

Fig. 6. (Lower) Tough-Pitch Copper at 100 X. The spaces left by the decomposition of Cu_2O have been enlarged by the persulphate.

A Rotating Table Carries the Molds

The molds are brought successively under the pouring spout by the mechanical manipulation of the rotating table, the operator acting both as pourer and table manipulator. Before pouring, the molds are filled with the controlled atmosphere or gas which is lighted at the bottom of the mold to insure its presence and which burns at the top during the entire pouring operation. A mold wash consisting of bone black suspended in water is sprayed into the molds, which, of course, are allowed to dry before use.

Each mold is emptied of its solid shapes when the table has revolved to a position 180 deg. from the point where the mold was poured. By this time the oxygen-free copper has cooled below redness. On opening a small door at the bottom of the mold cavity containing the solid metal, the shapes fall into a large tank of water where they are completely cooled.

A mechanical conveyor removes the shapes from the tank to the inspection bench and then to the saws. The tops of the various shapes are cropped because of the shrink hole present, which is indicative of sound, gas-free metal and is a characteristic of oxygen-free copper.

Routine Regulatory Tests

Not many routine tests are necessary to control this continuous process. An important one consists of watching the oxygen content of the metal as it flows from the reverberatory furnace,—it is kept at a range of 0.03 to 0.05 per cent O_2. This is accomplished by taking frequent samples of the metal and examining it under the microscope. The characteristic structure of tough-pitch copper is easily recognized and is shown in one of the photomicrographs. Another test consists of density determinations of full-size shapes by ascertaining the loss of weight in water compared to the weight in air.

A very interesting test, which demonstrates some of the qualities of OFHC as compared with tough-pitch copper, is regularly conducted on samples taken from finished shapes. These are forged and drawn into wire about 0.08 in. in diameter. Portions of this wire, after electrical conductivity determinations have been made, are annealed in a special laboratory furnace in hydrogen at 850 deg. C. (1560 deg. F.) for 30 min., quenched in water and subjected in a special machine to a reverse bend test of 90 deg. over a radius 2½ times the diameter. OFHC copper must stand at least 10 reversals before breaking. Reversals up to 12 to 15 are common. Tough-pitch copper, subjected to the same test, usually breaks after one reversal.

This is the metallurgical story of OFHC or oxygen-free, high conductivity copper. A discussion of its properties in comparison with those of phosphorized and tough-pitch coppers is not possible here. Two papers[1, 2] have been published which afford information of this nature.

The process described here is intensely interesting especially when seen in operation, and is at the same time simple. OFHC copper has been on the market about five years and is being shipped to nearly all fabricators in this country and large quantities are going abroad.

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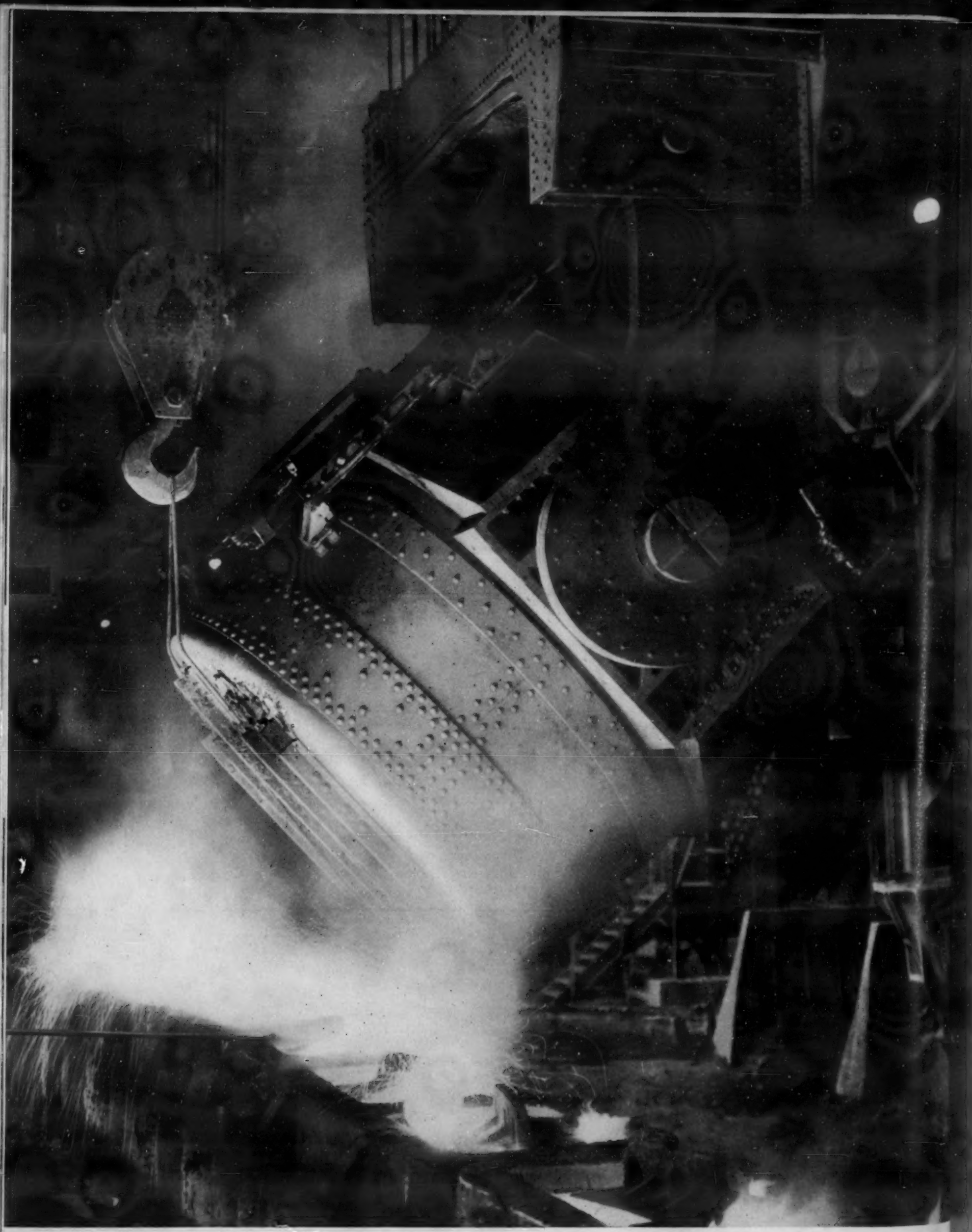
[1] W. R. Webster, J. L. Christie and R. S. Pratt. "Comparative Properties of Oxygen-Free High-Conductivity, Phosphorized and Tough-Pitch Coppers." *Proceedings*, A.I.M.E., Institute of Metals Div., Vol. 104, 1933, page 166.

[2] Sidney Rollé and P. H. Brace. "Oxygen-Free High-Conductivity Copper: Its Properties and Uses." *Mining and Metallurgy*, Vol. 14, 1933, page 340.



Courtesy Climax Molybdenum Co., New York

After the Pouring of a Large Open Hearth Heat

Steel Reminiscences—II

(Continued from the January Issue)

by Henry D. Hibbard

Consulting Engineer, Plainfield, N. J.

IN 1879 I ENTERED the employ of the Nashua Iron & Steel Co. at Nashua, N. H. The plant comprised a steel furnace, forge, scrap and bar mill and a small three-high blooming mill attached to the scrap mill.

I had there a varied experience practically unattainable today, I was nominally chemist but draftsman also; there was no other engineer. Then I helped sometimes as weight estimator of forgings, and also as shipping clerk.

Primitive Methods of Chemical Analysis

Methods of chemical analysis were then quite primitive. When I started there it took me two days to make a determination of phosphorus in iron, but before I left the laboratory I could do it by another method in one day—that is, I could get the result the same day I started it. Many years later I spoke of this to F. A. Emmerton who went as chemist to the Joliet Steel Co. at Joliet, Ill., in 1871. He said that when he began it took him a week to determine phosphorus in iron, to which no objection was made. Joliet made Bessemer steel rails profitably.

Soon after my arrival at Nashua in 1879, an electric lighting plant consisting of two direct-current arc lights was installed. It was before the time of alternating currents and of incandescent lights. The electric generator was driven by a belt. The man who came to set up the plant got caught by the belt and his arm was broken. So I was assigned to help him and, under his direction, did the wiring. I knew how to join two wires which astonished him. One of the lights was put into the steel plant, and one in the plate mill. The light they gave was far better than the kerosene torches then in use for night work.

The First Engineering Job

My first engineering job, soon after my arrival at Nashua, was to locate a new heating furnace for the bar mill. It was a recuperative furnace, designed by Sweet of Syracuse, N. Y. The air for the fire was heated by passing through hollow bricks built into the neck. The boss-mason said casually: "Just give me the location of the first casting, and I will do the rest." Even then I saw that, to do that, the whole furnace had to be considered. In time I studied it out and the furnace was built in the right place.

With the foreman of the plate mill I designed and drew an attachment for that mill for turning and dressing the rolls in place, as we had no roll lathe. It was driven by the mill engine and worked satisfactorily. I also designed tables for the blooming mill—not with driven rollers, however.

Blue printing was just coming in and I made prints of my latest drawings. Blue print paper was not then on sale anywhere. I made my own from a recipe obtained from Fred Daniels of Washburn & Moen, wire manufacturers of Worcester, Mass. I had a printing frame with plate glass and printed only by sunlight. The prints were poor, judged by modern standards, but serviceable. Incidentally, Washburn & Moen put in the first successful continuous rolling mill ever built, it was for making wire rods from 4 in. x 4 in. billets.

An Early Steel Melting Furnace

In time, as my superiors left, I was promoted to be foreman of the steel plant. There was one 10-ton steel furnace, the largest size then built. The hearth was acid, of course, made of sand, for, though the basic process had just been invented, it was not practiced anywhere. The roof and upper part of the furnace were built of imported Dinas silica brick. Such brick were not then made in this country. The steel ladle was supported by a swinging but not lifting crane and there was a 15-ton jib ingot crane, hydraulic, of course, for handling the ingots. All ingots except a few large ones, noted later, were bottom-cast. We made rectangular or slab ingots for boiler-plates, cylindrical ingots for forgings, and short cylinders for locomotive driving wheel tires.

The name "open-hearth" was not then applied generally to such furnaces. To me it has always seemed that a Siemens-Martin regenerative steel-melting furnace should have a short distinctive name commemorative of the inventors. I recommended the name "siema" which I use in my own notes. It is made up of the first syllable of the name of each inventor—Siemens of the furnace and Martin of the process.

The Melting Stock Used

The melting stock, all low phosphorus, was pig iron, our own scrap, and wrought iron blooms. A little miscellaneous purchased steel scrap was also used but sparingly, as its phosphorus content was unknown. Only Martin

steel was made, so no excess of pig was used. We had a pile of Mokta iron ore from Algeria but did not use it as we did not know how to do so properly, and oxygen was our *bête noire,* to be kept out of the bath metal in every possible way.

Our pig iron was either Swedish or English. The Swedish, which was smelted with charcoal, was in flat cakes or slabs. Its phosphorus was low and sulphur almost nil. Some brands contained 3 per cent or more of manganese, and the iron was often white in part or mottled. The English iron, in pigs of ordinary size and shape, had relatively little manganese.

The wrought iron blooms were made in Northern New York, direct from ore, in Catalan forges. In such a furnace the ore was reduced to metal in a deep charcoal fire. They cost over $50 per ton.

Charging the 10-Ton Open-Hearth

An initial charge of pig iron and scrap, some six tons in weight, was charged and melted. Then the blooms, preheated red hot in another furnace, were fed to it in batches of about ½ ton each until all was charged. The bath boiled as soon as melted. The blooms, which floated in it until melted or dissolved, always contained some oxide of iron or unreduced ore, and so caused some oxidation of carbon as well as dilution, and the bath was never quiet. But, on the other hand, the boil was never brisk or strong as is customary at times when ore is added plentifully as in the excess-of-pig method, now usually practiced.

The slags were vitreous when cast in a thin cake on the iron floor. The fracture was olive green or yellowish depending, I think, on the proportion of manganese in the melting stock. The more manganese the greener the slag from the silicate of manganese it contained.

Two heats of steel were made each week day or 12 per week. The night shift started about 11 o'clock and their heat was usually tapped about 7 o'clock the next morning. The day turn then came on and their heat was finished about 5 o'clock that afternoon. Between heats, and through week-ends the gas-maker ran the furnaces to keep them hot. It was thought best for each melter to make a complete heat so as to fix the responsibility for each. Costs were consequently high.

I aimed to be present at the finish of every heat to analyze the samples and then to calculate the final additions. I had a telephone in my room and the night watchman called me in the early morning, usually about 5 o'clock, when the heat was nearly ready. As a rule I was the first person to travel the road to the steel plant each morning. When it had snowed in the night I broke my own path through the drifts.

Preliminary Analyses for Carb. Man.

I had short color methods for analyzing the metal for carbon and manganese while the charge was in the furnace. My sample was a small cake poured on the iron floor. If its carbon was high or over 0.25 per cent, it was promptly moved, to break its close contact with the cold iron, and so to prevent rapid cooling which, by holding carbon in the hardening state, tended to give too low a result.

The drillings, both of the standards and sample, were quickly weighed on a glass spring balance. A weakly magnetized knitting needle handled the drillings.

For carbon, drillings were dissolved in nitric acid, boiled until the brown fumes disappeared, and then compared, without dilution, with two other standards, one higher in carbon and one lower, treated in the same way at the same time. It was easy to tell which standard it was nearer to than to the other and how much nearer. Three or even more standards could be used when there was doubt as to the probable carbon content in the metal.

For manganese a little more time was required. The nitric acid solution was, after the brown fumes were boiled off, diluted to double the quantity, and then given an addition of peroxide of lead. That, with further boiling, converted the manganese into permanganic acid, whose pink color, after the lead had settled, told by its intensity, the manganese content. It could be compared with other samples, one higher in manganese and one lower, treated in the same way. Actually I rarely used standards as the bath metal seldom had over 0.03 per cent at the end, and I could tell without a standard whether it had 0.01, or 0.02, or 0.03 per cent or none at all.

All additions to the charge to rectify the composition, either spiegel, ferromanganese or pig iron, were made in the furnace, being placed on the banks and allowed to begin to melt, when they were pushed into the bath, which was then stirred. This method took some time and effort, but made for good quality, because of the time afforded for the metal to clean itself.

We had no testing machine. A sprue of each heat was forged down to flat bar ⅜ in. thick, which was bent cold. All soft steel bent 180 deg. The harder steels broke and the angle of flexure before breaking was recorded.

For working steel there was a plate mill, a forge plant, tire mill and the small blooming mill mentioned. In the forge were some helve hammers, some direct-acting, the largest having a 10-ton trip. There was none larger in the country.

Plate Rolling

The plate mill had two stands of rolls, two-high. All plates were rolled twice. The first, or roughing rolling, reduced the ingot to a slab about 4 in. thick, which if too large for a single plate, was nicked across hot by chisel and sledge at the proper place to give the weights desired. When cold these slabs were broken at the nick under a drop. We had no bloom shears. Heating for the second rolling was higher—to a wash heat which melted the scale on the slabs. This gave a new surface to the plate. Because of this method, or for some other reason, no case of a pitted or redshort plate ever came to my notice there. I doubt strongly if there was ever one.

Shortly after that time Samuel T. Wellman, at the Otis Steel Co. in Cleveland, introduced the method of rolling plates at one operation from ingot to finished plate. This demanded that the ingot should have a thick skin free from skinholes. To secure this the steel must rim in the mold without rising much, preferably not any.

Casting Cylindrical Ingots

Cylindrical forging ingots were cast in sheet iron cans placed within strong iron casings with a space of 2 or 3 in. between the can and the outer shell. This space was filled with dry sand. Fluted ingots had not then been invented. For small ingots up to about 18 in. diameter, the outer casing was built up of a number of reinforcing iron hoops, each of which had strengthened the breech of a Parrott rifled cannon used in the Civil War. For larger ingots up to 36 in. diameter, old cylindrical boiler shells were used.

We made ingots up to 27,000 lbs. in weight for large shafts. These were at first partly bottom cast—about one-third—the remainder being filled from the top. Each ingot had a smaller top section to which the porter-bar was clamped for handling it during forging. To lift such an ingot from the casting pit, the hydraulic pressure of the accumulator was not enough. So the accumulator was shut off and the pump sent its water directly to the cylinder of the ingot crane.

These largest ingots were made only in winter when there was sledding. To transport one to the forge shop, a sled of heavy timbers was built and drawn by eight big horses.

Some of the Troubles Met With

These big forgings were not always satisfactory. We knew nothing of heat treatment or of annealing such pieces; and nothing also of how to provide a sinkhead to furnish liquid metal to fill the pipe, in part at least, as the metal shrank and sank during freezing. So the upper central part of the ingot was unsound. Then the designers did not know their part well, for some of the shafts, long and relatively slender, as for the axles of stern-wheel steamboats on the Mississippi River, broke in service.

Then we had trouble from longitudinal cracks in these big ingots cast in cans. The expansion of the sheet iron forming the can from the heat of the molten steel caused it to buckle and so to form longitudinal wrinkles. Along the bottom of such a wrinkle a crack was likely to be developed in forging. Our sheet iron worker, who made the cans, was ingenious and he devised a slip joint running the whole length of the can to take up the expansion. That avoided the trouble nicely in large forgings thereafter.

Ammonia Gas Detected

Many of the large shafts were rough-turned and centered before being shipped. One day in the machine shop a machinist, engaged on such work, asked me why we put hartshorn in the steel. In reply to questions, he said he often smelled ammonia coming from the center of the end of a forging, usually a shaft, either when he centered it or when he knocked off the first center for recentering it after rough turning.

Soon after that he called me to such a shaft in his lathe, and I plainly smelled ammonia coming from a small fissure in the end of the shaft. He said that sometimes there was enough ammonia gas to escape with a hissing sound and to bring water to the eyes of all who were near.

As I recall the matter I cannot say whether the cavity which contained the gas was a pipe, or one opened up by forging with a too light hammer, but from its irregular shape I am inclined to think it was the latter. A wire could be inserted 2 in. Our forging steel had usually about 0.35 to 0.40 per cent carbon. I do not know whether or not rimming steel contains any perceptible quantity of ammonia. It may be characteristic of only killed or partly killed steels.

(To be continued)

Editorials

(Continued from page A27)

horses on the farm, and crowds out steam on the high seas.

Metals and alloys are an essential factor in this development. Besides the conventional products of a metallic nature used in building Diesel engines, there has recently been introduced some of the new low-alloy high-elastic steels for special parts, such as crank cases and bed plates where welding has proved successful. And in crankshafts, alloy gray irons have been incorporated with marked success.

The Diesel engine has attained maturity only very slowly. It is only in recent years that its use has expanded. It is stated that in 1932, sales amounted to less than 100,000 horse power. The 1934 sales had gone to 750,000 horse power, practically double the pre-depression peak. In 1935 that peak was almost trebled and for 1936 reliable estimates place total sales at over 2,100,000 horse power. Compared with automotive horsepower of 500,000,000 this is significant in the words of Charles Kettering.

As this development proceeds, there will be a still greater demand for new alloys and metals, enabling the designing engineer both to lighten the weight of the unit and increase its strength and efficiency. The Diesel field promises to be a source of expanding demand for metals and alloys.—E.F.C.

A German-English "Pony"

In honor of the meeting of the British Iron and Steel Institute in Düsseldorf, the Sept. 17 issue of *Stahl und Eisen* is bi-lingual. All the articles are in German on the left side of the page and in English on the right. This applies not only to the Iron and Steel Institute papers, but to everything in the text, even to abstracts and patent notes. Most of the advertisements also have both German and English text.

The 440 pages of this issue thus make a remarkable text book for home study of metallurgical German. The translation is as literal as will make good English or German. The articles cover many different branches of ferrous metallurgy, so that the student could prepare his own German-English dictionary from this issue and not miss much of the necessary vocabulary for general metallurgical reading.

While the object of the large amount of labor put into the translation was doubtless to make a special gesture of friendliness toward England to offset the disgust most English-speaking people have for the Hitler régime, and making a text book for metallurgical students was probably not aimed at, the result is one that American metallurgists might well make use of.—H. W. G.

Effect of Titanium

ON SOME PROPERTIES OF

17.5% Chromium Steel

by G. F. Comstock and C. L. Clark

Metallurgist, Titanium Alloy Mfg. Co., Niagara Falls, N. Y., and Research Engineer, Dept. of Engineering Research, University of Michigan, Ann Arbor, Mich.

THE PURPOSE of this investigation was to determine the influence of titanium additions on certain of the physical characteristics of a steel of the 17.5 per cent chromium type containing 0.20 to 0.30 per cent carbon. Four analyses were considered, which were prepared in the high frequency induction furnace at the University of Michigan and, as indicated in Table I, differed primarily in the titanium treatment and in the amount of titanium contained.

These steels were melted in magnesite crucibles in heats of approximately 25 lbs. Low carbon boiler punchings and ferro-chromium, containing a maximum of 0.20 per cent carbon, were used as the melting stock with the killing being done with silicon and aluminum before the titanium additions. For killing each heat before the titanium addition, 25 grams of 80 per cent ferro-silicon and 10 grams of aluminum were used. No attempts were made to keep the bath covered with slag during the melting operation but the slag which was produced was removed before the titanium addition. The values given in Table II show the losses encountered during the melting operations.

The heats were poured, at a temperature of approximately 2950 deg. F. into cast iron molds, the resulting ingots being rectangular and tapered possessing a cross section at the larger end of 2½ in. square. These ingots were then forged into ⅞ in. round bars.

Brinell Hardness Tests

Brinell hardness tests were made on these steels as forged and, after annealing for 2 hrs. at various temperatures, followed by slow cooling in the furnace. The results of these tests are presented in Table III, and show that the steels containing over 1 per cent titanium did not require annealing for softening after forging.

Before making other tests, Steels A, B, and C were annealed at 1650 deg. F., and Steel D was annealed at 1550 deg. F. Short-time tensile tests were then made in duplicate at room temperature, and at 1000 deg. F., 1200 deg. F. and 1400 deg. F. Titanium did not seem to have a consistent effect on the tensile properties at room temperature after annealing, but at higher temperatures it improved the elastic properties, especially the proportional limit at 1000 deg. F. This is shown by the data presented in Table IV where each value is the average from two tests. Steel B, containing 0.3 per cent carbon and only 0.25 per cent titanium seems to have in general the best tensile properties.

Oxidation Tests

Oxidation tests were conducted in triplicate at 1200, 1400, 1600, and 1800 deg. F. using cylinders ¾ in. in diameter and ½ in. long, heated in an electric muffle for 1000 hrs. in still air. At the lower temperatures the gain in weight due to scaling was measured, but after the 1800 deg. F. treatment the scale was removed electrochemically and the loss in weight determined. The gain due to scaling at 1200 and 1400 deg. F. was negligible for all the steels, indicating a very high resistance to oxidation. Table V gives the results at 1600 and 1800 deg. F., showing a decided improvement due to titanium. The atmospheric attack on Steels C and D at 1800 deg. F., however, was localized, and rather severe at certain points, so that Steel B was perhaps as good as any in this respect for practical purposes.

Creep Tests

Creep tests were made on the four steels by a method which complied with the requirements of the A.S.T.M. Tentative Standard E22-35T. The temperature of the specimens was 1100 deg. F., and a stress of 6000 lbs. per sq. in. was applied for 1000 hours. The data were plotted in the usual form, and the rates of creep determined from these curves at two periods of the tests are shown in Fig. 4 and tabulated in Table VI.

Table I.—Titanium Treatment and Analyses of the Steels Used

Steel	Kind of Ferrotitanium Added	Chemical Analysis C	Cr	Mn	Si	Ti
A	None	0.22	17.85	0.57	0.38	
B	19% Ti, 4% C	0.30	17.75	0.70	0.91	0.25
C	23.4% Ti, 0.01% C	0.21	17.27	0.68	0.77	1.11
D	39.45% Ti, 0.7% C	0.22	17.65	0.69	0.77	1.97

Table II.—Analysis of 17.5 Per Cent Chromium Steels Containing Titanium

	Added	Reported	Loss
Steel A			
Carbon	0.173	0.22	—0.047*
Chromium	17.50	17.85	—0.35
Manganese	0.63	0.57	0.06
Silicon	0.41	0.38	0.03
Steel B			
Carbon	0.298	0.30	—0.002*
Chromium	17.50	17.75	—0.25
Titanium	0.845	0.25	0.595
Steel C			
Carbon	0.173	0.21	—0.037*
Chromium	17.50	17.27	0.23
Titanium	1.55	1.11	0.44
Steel D			
Carbon	0.173	0.22	—0.047*
Chromium	17.50	17.65	—0.15
Titanium	2.29	1.97	0.32

* Gain in carbon content believed to be due to carbon variations in the ferrochromium used.

Table III.—Brinell Hardness After Annealing

Annealing Temp., Deg. F.	Steel A	Steel B	Steel C	Steel D
None; as forged	418	460	137	137
1450	220	225	149	140
1550	194	207	143	133
1650	165	181	134	130
1750	157	179	134	134

Table IV.—Results of Short-Time Tensile Tests

Steel	Temperature of Test, Deg. F.	Lbs. per Sq. In. Proportional Limit	Yield Stress at Deformation 0.1%	0.2%	Tensile Strength	Per Cent Elong. in 2 In.	Red. of Area
A	85	30,000	42,000	43,125	80,650	29.25	55.35
B	85	32,500	52,500	54,250	90,475	24.00	47.30
C	85	30,000	44,750	47,000	75,425	26.50	44.25
D	85	26,250	42,500	44,750	71,925	23.00	41.45
A	1000	9,500	22,375	24,750	46,650	27.00	57.30
B	1000	18,000	31,875	34,625	55,000	29.50	58.80
C	1000	15,500	23,500	24,750	38,925	32.00	65.95
D	1000	18,000	25,250	26,250	42,300	31.50	60.95
A	1200	4,500	12,500	14,250	24,400	49.50	79.90
B	1200	4,750	11,875	14,125	24,500	50.25	86.20
C	1200	5,000	11,875	12,875	20,425	52.75	82.45
D	1200	6,000	12,000	13,250	20,575	46.75	77.20
A	1400	0	5,750	6,750	11,400	77.00	92.10
B	1400	0	5,375	6,500	13,050	60.03	94.60
C	1400	0	5,750	6,875	10,400	72.50	92.65
D	1400	0	6,250	7,250	10,875	72.00	88.85

Table V.—Change in Weight After 1000 Hours Heating in Still Air

Temperature of Test, Deg. F.	Gain, Grams per Sq. In., Scale Left On Steel A	Steel B	Steel C	Steel D
1600	0.0760	0.0017	0.0083	0.0085
1600	0.0611	0.0043	0.0071	0.0142
1600	0.0407	0.0046	0.0129	0.0136
Average	0.0593	0.0035	0.0094	0.0121
	Loss, Grams per Sq. In., after Removing Scale			
	Steel A	Steel B	Steel C	Steel D
1800	0.7645	0.6160	0.8590	0.2455
1800	1.1765	0.4765	0.3565	0.1452
1800	0.7588	0.8050	0.8800	0.3965
Average	0.8999	0.6325	0.6985	0.2624

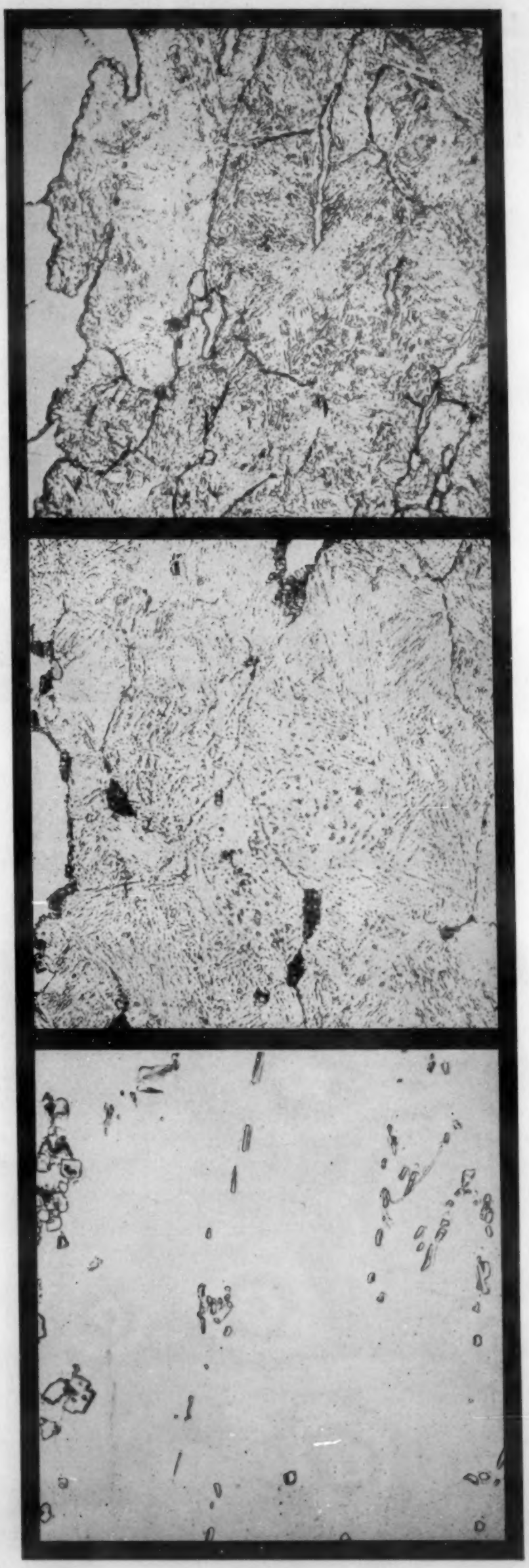
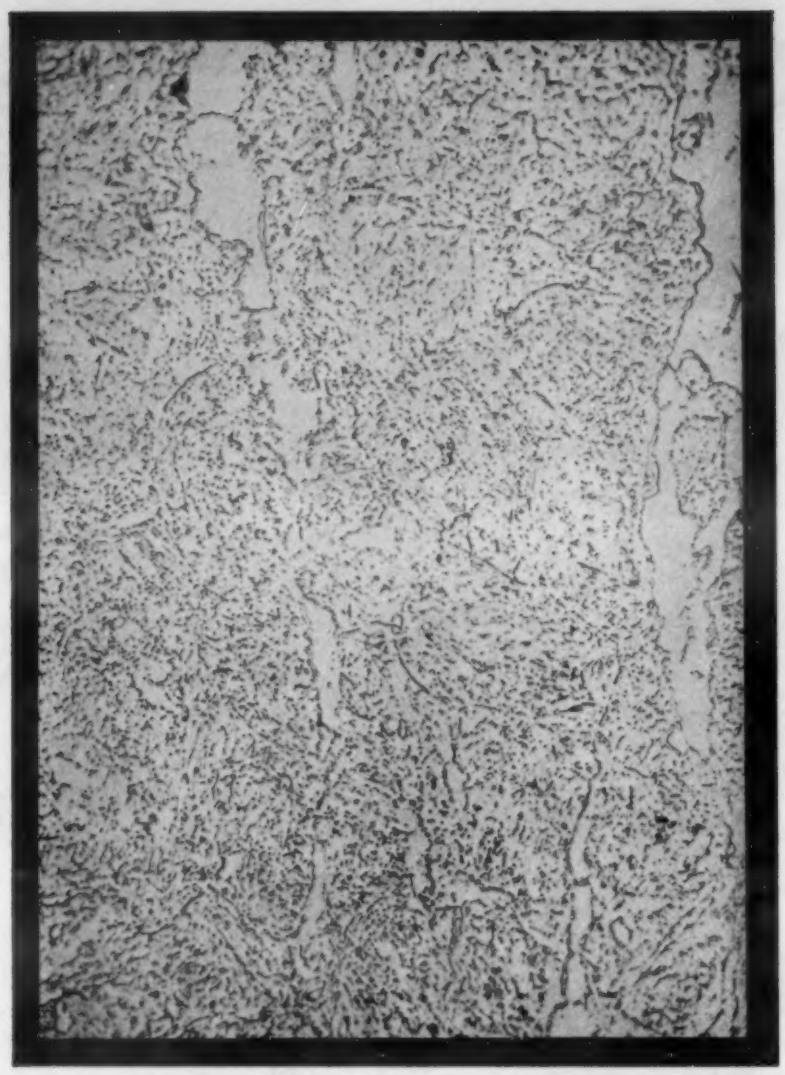


Fig. 1. (RIGHT)—*Microstructures of Cr-Ti Steels at 500 Diameters in the As Forged Condition.*

Top: Steel A—0.22 C, 17.5 per cent Cr. Brinell 418.
Center: Steel B—0.30 C, 0.24 Ti, 17.5 per cent Cr. Brinell 460.
Bottom: Steel D—0.22 C, 1.97 Ti, 17.5 per cent Cr. Brinell 137.



Steel A—0.22 C, 17.5 per cent Cr. Brinell 165.

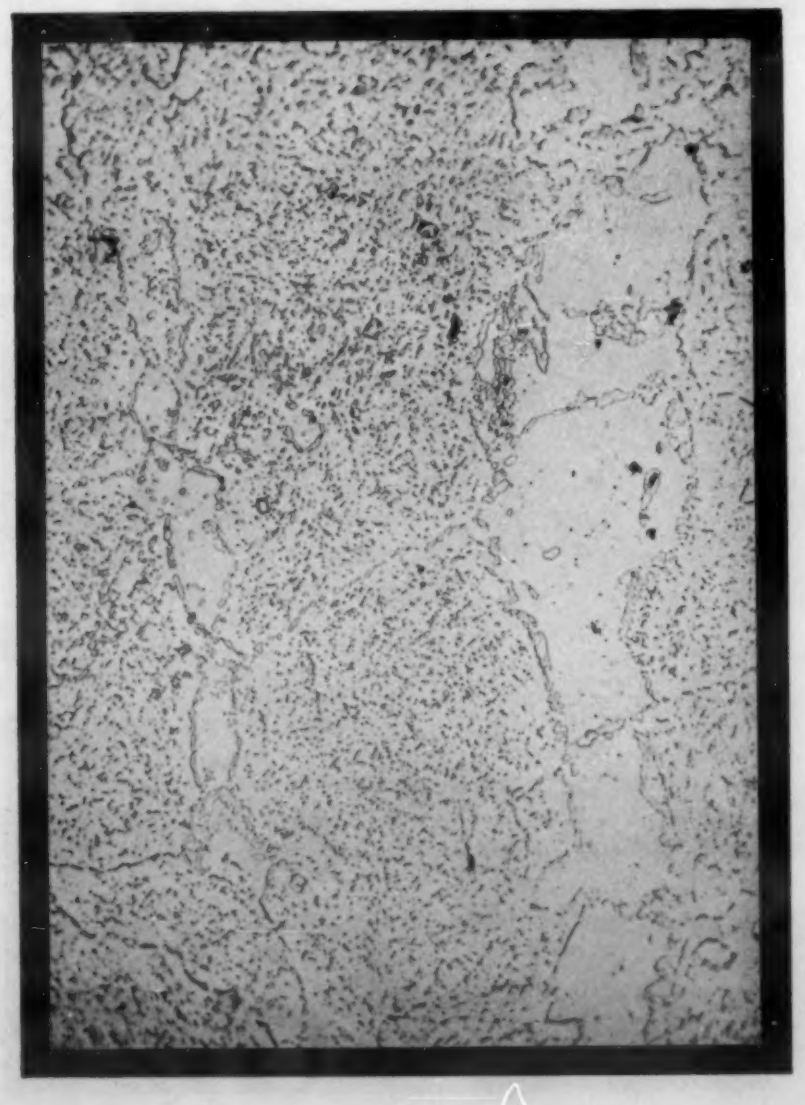
Table VI shows decided differences between the four steels, steels C and D having entered the stage of increasing creep rate in less than 800 hours, while for steel A and B the creep rate was still constant. Steel C was apparently near failure at the termination of the test, and was decidedly lower in creep resistance than the steels with both less and more titanium. Steel B, showing the best creep resistance, was decidedly higher in carbon than the others, and had only a moderate titanium content, so that the ratio of Ti to C in it was less than is required to avoid air hardening or than is usually suggested for stabilizing structure.

After the creep tests were finished the specimens which had been subjected to a stress of 6000 lbs. per sq. in. for 1000 hrs. at 1100 deg. F. were tested in tension at room temperature to determine the effect of the high temperature treatment. The results are compared with the original tensile properties of the respective steels in Table VII.

Some of the data for Steel C in Table VII are missing because the specimen broke at the shoulder, having been strained nearly to failure in the creep test. It appears from Table VII that while the properties of the non-titanium Steel A were all impaired by the creep test, those of the titanium Steel B were all improved, and the titanium Steel D was also improved in ductility. After creep testing, the titanium Steels B and D showed decidedly better ductility than the non-titanium Steel A. Thus it appears from these tests that titanium improved the ductility of the steel after subjection to load at high temperature.

Fig. 2. Microstructures of Cr-Ti Steels at 500 Diameters. Annealed at 1650 deg. F.

Steel B—0.30 C, 0.24 Ti, 17.5 per cent Cr. Brinell 181.



Steel D—0.22 C, 1.97 Ti, 17.5 per cent Cr. Brinell 130.

Table VI.—Comparative Creep Resistance at 1100 Deg. F. Under a Stress of 6000 Lbs. per Sq. In.

	Rates of Creep, Per Cent per 1,000 Hrs.			
	Steel A	Steel B	Steel C	Steel D
After 400 hrs.....	0.295	0.265	1.11	0.46
After 800 hrs.....	0.295	0.265	3.98	0.68

Table VII.—Tensile Properties at Room Temperature Before and After Creep Tests

		Lbs. per Sq. In.				Per Cent	
		Proportional	Yield Stress at Deformation				
Steel	Condition	Limit	0.1%	0.2%	Tensile Strength	Elong. in 2 In.	Red. of Area
A	Original	30,000	42,000	43,125	80,650	29.25	55.35
A	After Creep	25,000	40,250	41,250	77,400	19.00	24.80
B	Original	32,500	52,500	54,250	90,475	24.00	47.30
B	After Creep	32,500	56,500	58,000	93,950	25.00	49.20
C	Original	30,000	44,750	47,000	75,425	26.50	44.25
C	After Creep	25,000	40,000	41,250	.....	....	....
D	Original	26,250	42,500	44,750	71,925	23.00	41.45
D	After Creep	22,500	41,000	43,500	71,950	30.00	46.50

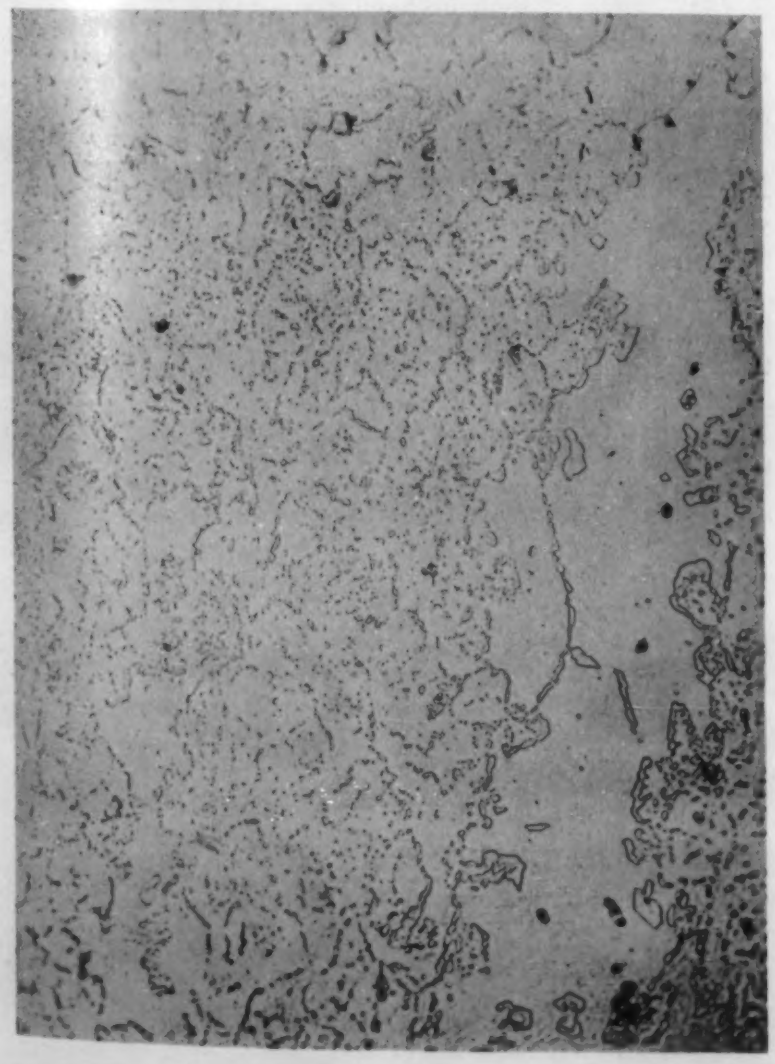
Microstructures Examined

The microstructures of these steels were examined after various treatments, and those of Steels A and B were quite different from those of Steels C and D. The latter were all practically the same for both steels in all conditions, showing merely ferrite with titanium cyanonitride crystals. Steels A and B showed martensitic structures as forged and, when annealed, this changed to a spheroidized carbide structure with some ferrite banding. The structures of these two steels did not differ very much until after the creep tests. Then Steel B, containing titanium, was finer grained and showed a better distribution of the carbides

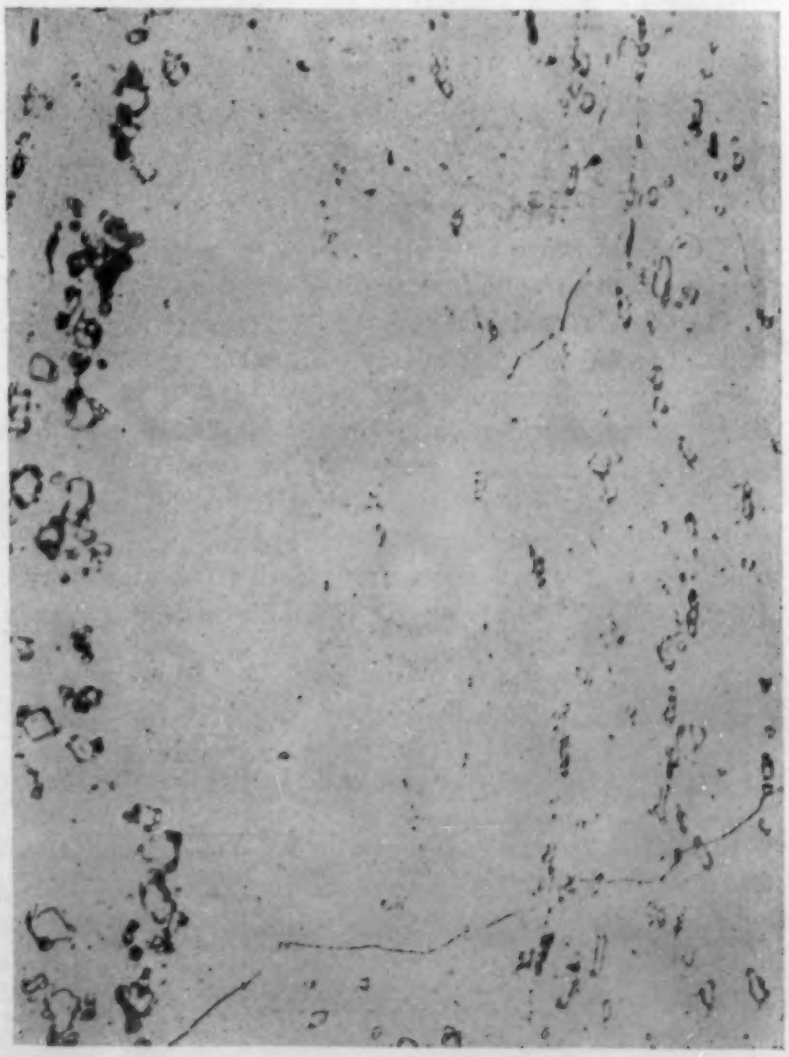
Steel A—0.22 C, 17.5 per cent Cr.

Fig. 3. Microstructures of Cr-Ti Steels at 500 Diameters after 1,000 Hrs. at 1,100 Deg. F. under Stress of 6,000 Lbs. per Sq. In.

Steel B—0.30 C, 0.24 Ti, 17.5 per cent Cr.



Steel D—0.22 C, 1.97 Ti, 17.5 per cent Cr.



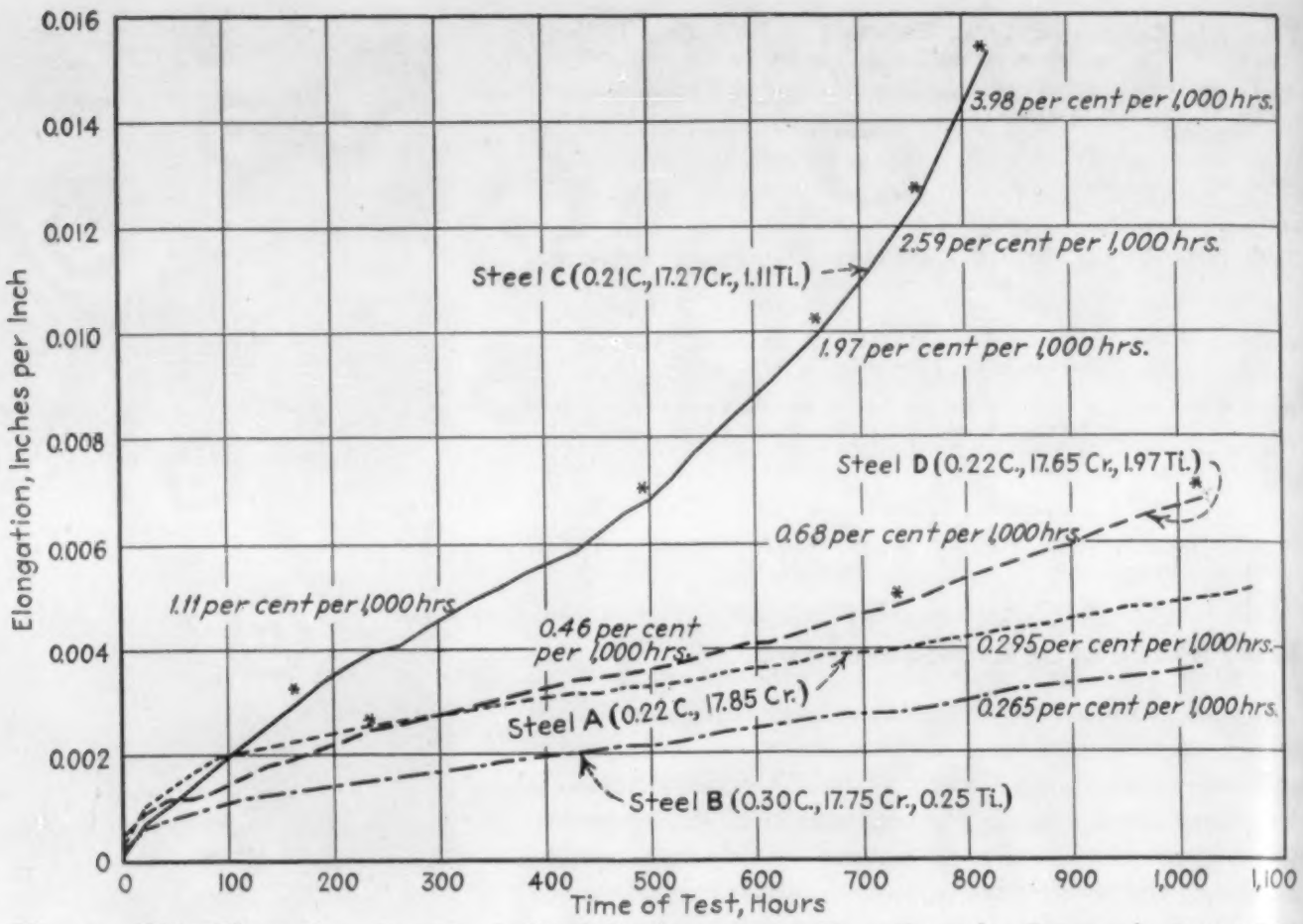


Fig. 4. Time-Elongation Curves of Cr-Ti Steels at 1,100 Deg. F. under Stress of 6,000 Lbs. per Sq. In.

than Steel A. Some photomicrographs are submitted to illustrate these structures, all having been taken at a magnification of 500 dia., and after etching with aqua regia and glycerine. The skillful work of J. W. Freeman in preparing these illustrations is gratefully acknowledged.

A further discussion of the hardness and structures of these steels in the ingot form and after various heat-treatments was presented at the 1936 A.S.M convention in Cleveland by R. E. Bannon, Research Associate, Metallurgical Research Laboratories, The Titanium Alloy Mfg. Co., Niagara Falls, N. Y.

Conclusions

The following conclusions seem to be justified by the results of these experiments:

(1) Steels containing about 17.5 per cent chromium and 0.2 to 0.3 per cent carbon with not over 0.25 per cent titanium require annealing to soften them below 200 Brinell after forging, but similar steels containing over 1 per cent titanium do not.

(2) The tensile properties of all these steels, forged and annealed, containing zero to 2 per cent titanium, were satisfactory at room temperature and at temperatures of 1000, 1200, and 1400 deg. F. Titanium seemed to improve some of the elastic properties at high temperature, and especially the proportional limit at 1000 deg. F.

(3) Titanium improved the resistance to oxidation at 1600 and 1800 deg. F. and 0.25 per cent seemed to be sufficient for a marked improvement at 1600 deg. F. With higher titanium the oxidation at 1800 deg. F. was localized.

(4) The steel with higher carbon and 0.25 per cent titanium showed the best resistance to creep under 6000 lbs. per sq. in. load at 1100 deg. F., but higher titanium contents impaired the creep resistance.

(5) Titanium improved the ductility of this steel after subjection to the creep test, the ductility of the titanium steel being increased by creep testing, while that of the non-titanium steel was lessened.

(6) The titanium additions increased the structural stability of these steels, for none of the alloys containing titanium showed as detrimental structural changes after creep testing at 1100 deg. F. as the plain chromium steel showed.

This investigation was sponsored as a research project by the Titanium Alloy Mfg. Co., Niagara Falls, N. Y., and the tests were conducted in the department of engineering research, University of Michigan, Ann Arbor, Mich. The thanks of the authors are due to both these organizations for permission to publish this report.

CONTROLLING A

"CONTROLLED ATMOSPHERE"

by A. E. Krogh *Engineer, The Brown Instrument Co., Philadelphia*

SO much is being written and said about controlled furnace atmospheres and their effects upon steels that it appears desirable to inquire into the methods of measurement used to gage such atmospheres. While there is widespread agreement that for best results in preheating, hardening, tempering, normalizing, carburizing, etc., special gas atmospheres should be maintained around metals undergoing any particular type of heat treatment, the agreement is considerably less as soon as the question of the proper atmosphere for any given metal or alloy is under consideration. This is not at all strange in view of the fact that a great many of the tests which are used as a basis for judgment have been quite incomplete or have been accomplished with very crude measurement. Few data are available to completely state the relative quantities of all gases present.

The reason for this situation undoubtedly lies in the difficulty of complete analysis of furnace atmospheres in the average heat treatment plant.

Many of the data available regarding the action of mixed atmospheres upon hot steel are based only upon a test for the carbon dioxide percentage in the atmosphere. The measurement of CO_2 is generally made by means of a manually operated chemical Orsat. Such units are very good for flue gas analysis, but they are hardly reliable for the accuracy required in heat-treating work, and are, of course, subject to grave errors if not constantly maintained in order. Some observers have used automatic Orsats of similar principle with somewhat better results. Naturally, such instruments are capable of making CO_2 analyses at much more frequent intervals and are reasonably consistent, if carefully supervised.

In recognition of the insufficiency of CO_2 data, many heat treaters have turned to the measurement of CO. This is nearly always accomplished through chemical absorption of the gas in acid or ammoniacal cuprous chloride, Cosorbent, or other chemical. All such solutions reach a saturation point rather quickly and, at best, the method is laborious. To achieve greater accuracy in the measurements, considerable laboratory apparatus is required in combination with the knowledge of a trained chemist. Measurements of H_2 CH_4, etc., have also generally been out of the question for the lack of both apparatus and training.

The logical result has been that many practical heat treaters have found it preferable to test atmospheres by the ancient, honorable, and expensive method of "cut and try." This method has the decided advantage of completeness in each instance, but very little else can be said in its favor. Perhaps the reason that many phenomena in the heat treatment of metals have been so puzzling lies in these conditions, which certainly are responsible for many conflicting reports received from various sources.

In attempting to remedy this situation, a series of tests have been undertaken to determine those characteristics of furnace atmospheres which can best be used as a means of measuring the conditions existing in a furnace, for it is a truism that to control, it is first necessary to measure. These tests have revealed considerable pertinent data which are now being published in response to a number of requests.

The Effect of Gases Upon Steels

The definition of the American Society for Metals for heat treatment is "An operation or combination of operations, involving the heating and cooling of a metal or alloy in the solid state for the purpose of obtaining certain desirable conditions or properties."

Unfortunately, the heating and cooling of a metal or alloy is also likely to produce some undesirable properties unless steps be taken to prevent it. Two particularly troublesome things that can happen to steel undergoing heat treatment are scaling and decarburization (or carburization). Both can be avoided by surrounding the steel with a fluid which will not react with the steel at any temperature reached. The problem is to find such a fluid for each condition. For some metals it is possible to employ molten baths of some sort, but this is frequently impractical.

It is not practical to avoid this problem by the use of pure inert gases due to their cost, so for production work some way of using a mixture of gases must always be found. This is usually accomplished by trial and error, and we need not here emphasize the undesirability of that method in terms of loss of time, material, and the temper of the boss. Even after a batch has been successfully treated one day, it is often necessary to partially repeat the trials during the following days, due to apparent vagaries of weather and furnace.

Oxygen, CO_2, H_2O, SO_2, and probably most compounds (except CO) containing oxygen are, in certain temperature ranges, strongly oxidizing to steel. Since complete or par-

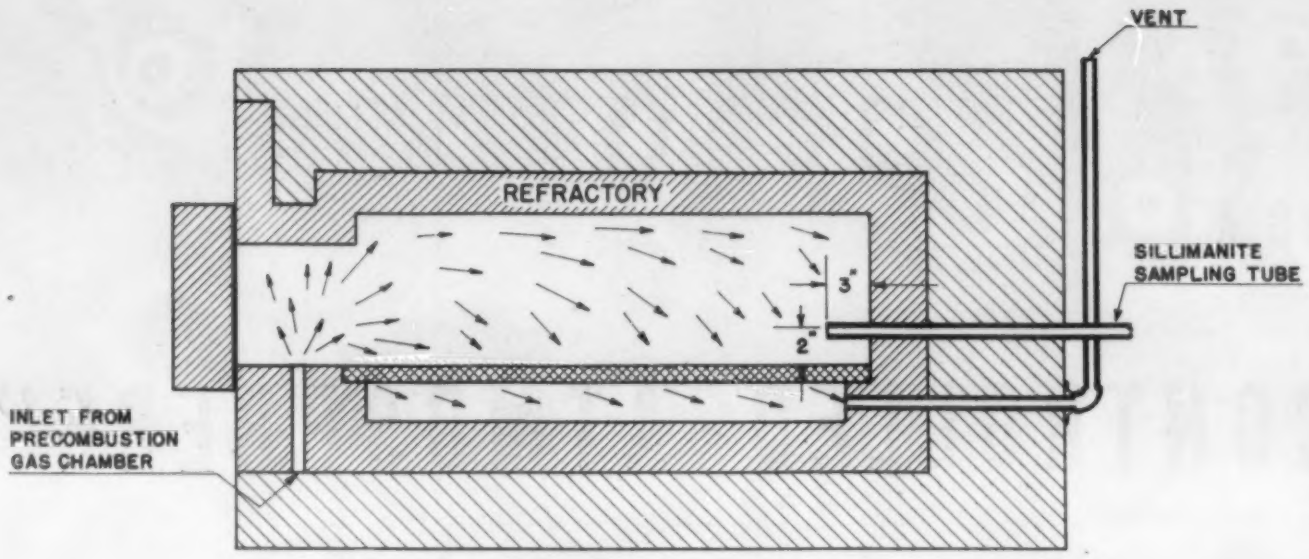


Fig. 1.—Partial Section of Electrically Heated Pre-Combusted Atmosphere Furnace Used in the Tests.

tial combustion of ordinary fuel always produces one or more of these gases and since air contains lots of oxygen, scaling would always occur in furnace heating were it not for the fact that certain other gases have an opposing tendency in regard to the steel—notable among these are carbon monoxide (CO) and hydrogen (H_2). The presence of the desired percentages of these gases will tend to neutralize the oxidizing effects of the others mentioned. There is, however, also the problem of carburization and decarburization to consider, and quite a different gas balance may be needed to avoid these effects than for the scaling problem.

In Table I is shown a tabulation of reactions of various gases with iron, cementite, and scale, and also some inter-reactions of gases. The list is necessarily partial, in that it enumerates only the gases commonly found in greatest quantities in heat-treating furnace atmospheres and omits the mention of SO_2, H_2S, formaldehydes, etc., although some of each is generally present.

Among the gases listed, O_2, CO_2, and H_2O will produce scale (FeO); O_2 and H_2O will further oxidize FeO into Fe_2O_3 and Fe_3O_4; CO and H_2 will remove oxygen from these oxides and are, therefore, known as "reducing"; i.e., these gases will tend to clean the steel. At this point it is probably well to point out that the terms "oxidizing" and "reducing," where used in this article, refer to the action of gases upon scale and should not be confused with similar terms generally used to designate complete and incomplete combustion respectively.

Carburization of iron will be caused by CO and CH_4, but O_2, CO_2, and H_2 will decarburize, and high carbon steels can be decarburized by CO as well.

All reactions are greatly accelerated at elevated temperatures, especially in the presence of water vapor. The various inter-reactions listed illustrate the complexity of the problem because as they occur, nascent atomic gases may contact the steel, and they are extremely active.

When studying Table I in the light of available literature, the following facts respecting common atmospheres derived by partial combustion of industrial gases appear outstanding:

1. Oxygen (O_2) produces scale and will decarburize steel. It is generally held to a minimum and ordinarily not found in excess of 0.3 per cent unless air infiltration is occurring.
2. Carbon monoxide (CO) will tend to remove scale and carburize the metal. It is frequently used in relatively large percentages (up to 16 or 18 per cent). High carbon steels can be decarburized by this gas.
3. Carbon dioxide (CO_2) will scale steel by dissociation, but it is not generally considered extremely active in this regard. It will also decarburize. It is always present (from 1 per cent up).
4. Hydrogen (H_2) will clean steel by deoxidizing the scale and will also decarburize, especially in moist atmospheres. (W. E. Jominy states that this gas in the presence of water vapor is the fastest decarburizing agent known to him. (*Transactions* American Society for Metals, Vol. 24, March 1936, pages 127-128.) It is usually present in large quantities.
5. Methane (CH_4) does not directly affect scale, although it liberates hydrogen in the process of carburization. It is present in large quantities at low air/gas ratios, especially at lower temperatures.
6. Water vapor (H_2O) is descaling. It is also a very active catalyst aiding the decarburizing gases. Some moisture is nearly always present, but modern atmosphere preparation machines are frequently adapted to remove a large proportion of this vapor before the mixture is admitted to the furnace.

Table 1.—Some Reactions of Some Furnace Gases with Iron, Iron Carbide, Iron Oxide, and Each Other at Elevated Temperatures

Name	Symbol	O_2	CO	CO_2	H_2	CH_4	H_2O
Iron	Fe	Oxide.	Carb.	Oxid.	X	Carb.	Oxid.
Iron Carbide	Fe_3C	Decarb.	X	Decarb.	Decarb.	X	X
Iron Oxides	FeO Fe_2O_3 Fe_3O_4	Oxid.	Reduc.	X	Reduc.	X	Oxid.
Oxygen	O_2	X	CO_2	X	H_2O	CO & H_2O	X
Carbon Monoxide	CO	CO_2	X	X	X	X	CO_2 & H_2
Carbon Dioxide	CO_2	X	X	X	CO & H_2O	X	X
Hydrogen	H_2	H_2O	X	CO & H_2O	X	X	X
Methane	CH_4	CO & H_2O	X	X	X	X	X
Water	H_2O	X	CO_2 & H_2	X	X	X	X
Nitrogen	N_2	X	X	X	X	X	X
Carbon	C	CO	X	CO	CH_4	X	X
Breaks Into		X	C & O_2	CO & O_2	X	C & H_2	H_2 & O_2

7. Nitrogen (N_2) is usually considered inert except in its nascent state. Some authorities, however, consider that a moist nitrogen atmosphere is actively decarburizing because of the presence of water vapor. It is, of course, always present in large quantities.
8. It appears that most authorities agree in the following conclusions:
   (a) CO_2/CO represents a ratio which, if large, will cause decarburization and scaling of steel. If very small, both of these actions will be reversed. In an intermediate range, carburization and scaling may occur simultaneously due to these gases.
   (b) CH_4/H_2 represents a ratio which, if large, will cause carburization of steel. If very small, this action will be reversed.
   (c) H_2O/H_2 represents a ratio which, if large, will cause scaling of steel. If small, this action will be reversed.

In controlling these ratios in the active zone of the furnace, several things have to be considered when a fuel gas is partly burnt with a deficiency of air, and partly cracked, as is the case in the preparation of the usual commercial atmospheres. Among these are the initial composition of the fuel gas, the humidity of the air, the gas/air ratio, the rate of flow, the temperature of the pre-combustion and cracking chamber, the presence or absence of catalysts there, the completeness of dehydration of the gas before it enters the furnace proper, the composition of the gas at this stage, the rate of flow, the temperature of the furnace, and the catalytic effect of the charge and the furnace walls.

After the fuel gas is chosen and the temperature of the furnace proper is fixed, the factors under most ready control are the gas/air ratio and the temperature of the pre-combustion chamber. As will be shown later, slight changes in the gas/air ratio, in the ranges usually employed, produce quite large changes in the composition of the exit gas from the pre-combustion chamber, so that the pressure gages always employed may not allow a sufficiently fine adjustment. Some other "tell-tale" which will allow finer adjustment, as well as information on the effect of the temperature of the pre-combustion chamber so that, if necessary, that may be adjusted also, would be advantageous in giving the furnace operator greater certainty that he was in reality duplicating a gas composition that he had previously found suitable for the work in hand.

An experimental program was undertaken to search for a suitable "tell-tale," and for the needed information.

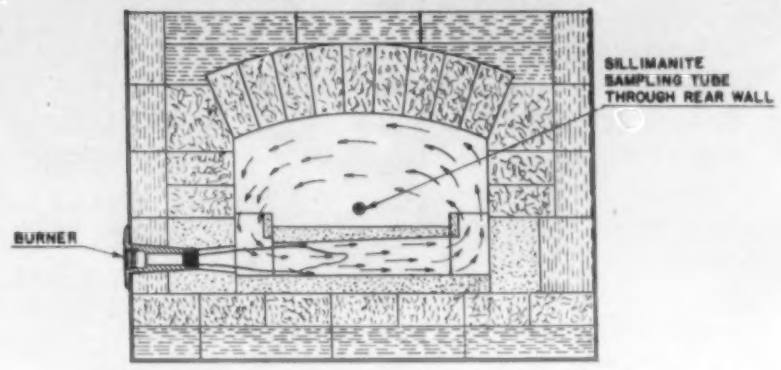
Outline of Tests

The purposes of the tests herein described were:

1. To determine the measurable properties of furnace atmospheres.
2. To determine the most significant of these.
3. To devise means of continuously measuring and recording this property.

In this work, two furnaces of different types were employed. It is believed that these are representative of general practice in industry. No work was handled in the furnaces during the tests. The data given in this paper were all secured by means of the electric furnace shown in Fig. 2, but much operating data have been secured on the gas-fired furnace shown in Fig. 1, wherein heat was supplied by combustion below the hearth and the resultant gases made to circulate around the work and the hearth.

Fig. 2—Sectional End View of Gas Heated Controlled Atmosphere Furnace.



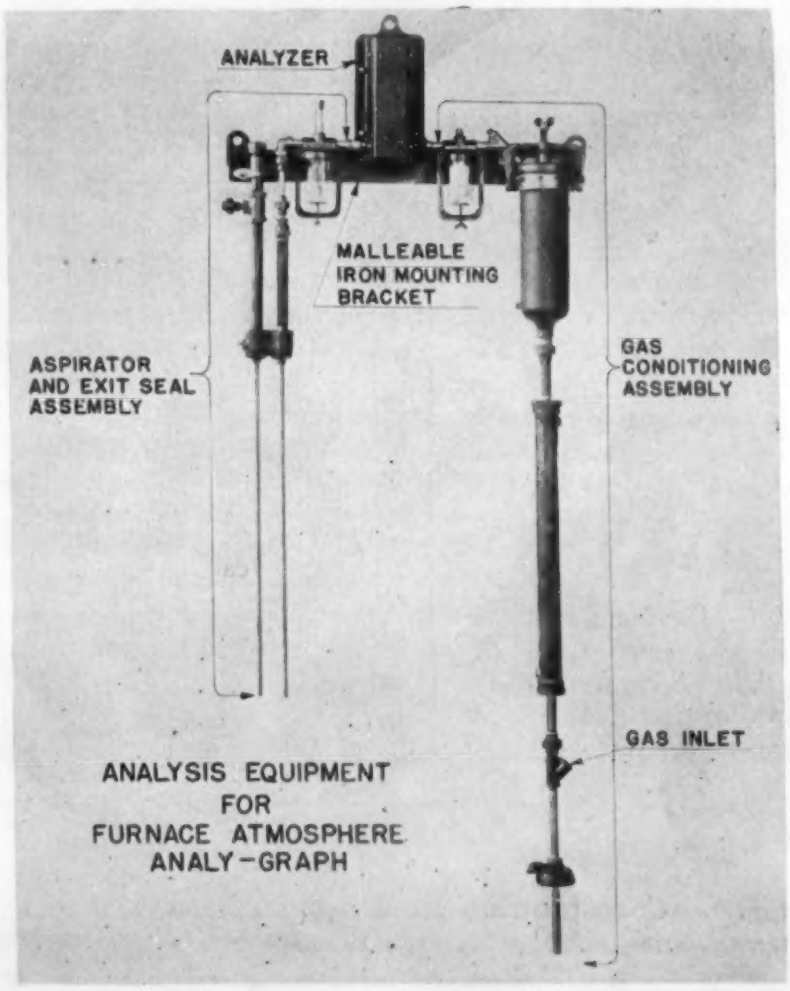
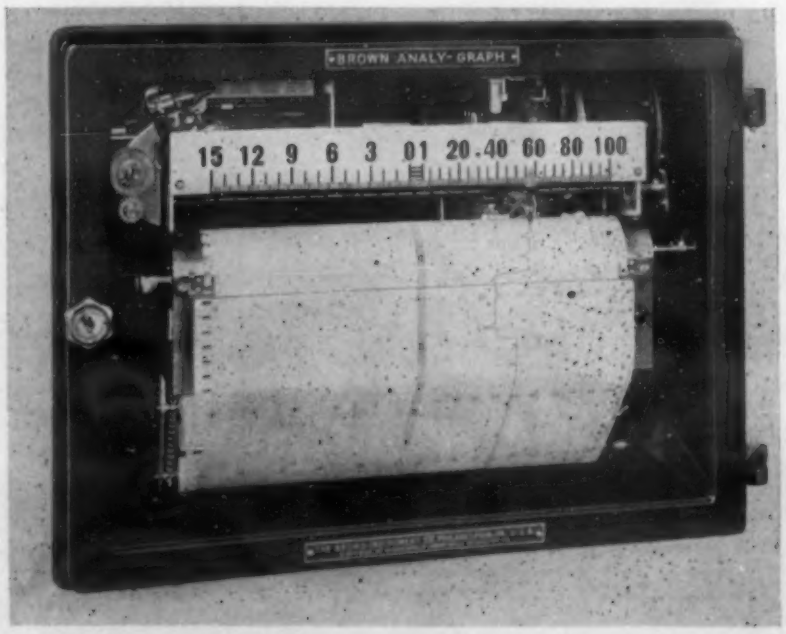


Fig. 3.—Analysis Equipment Used in Combination with Furnace Atmosphere "Analy-graph."

Fig. 4.—View of Instrument Used to Record Thermal Conductivity of Gas During Tests.



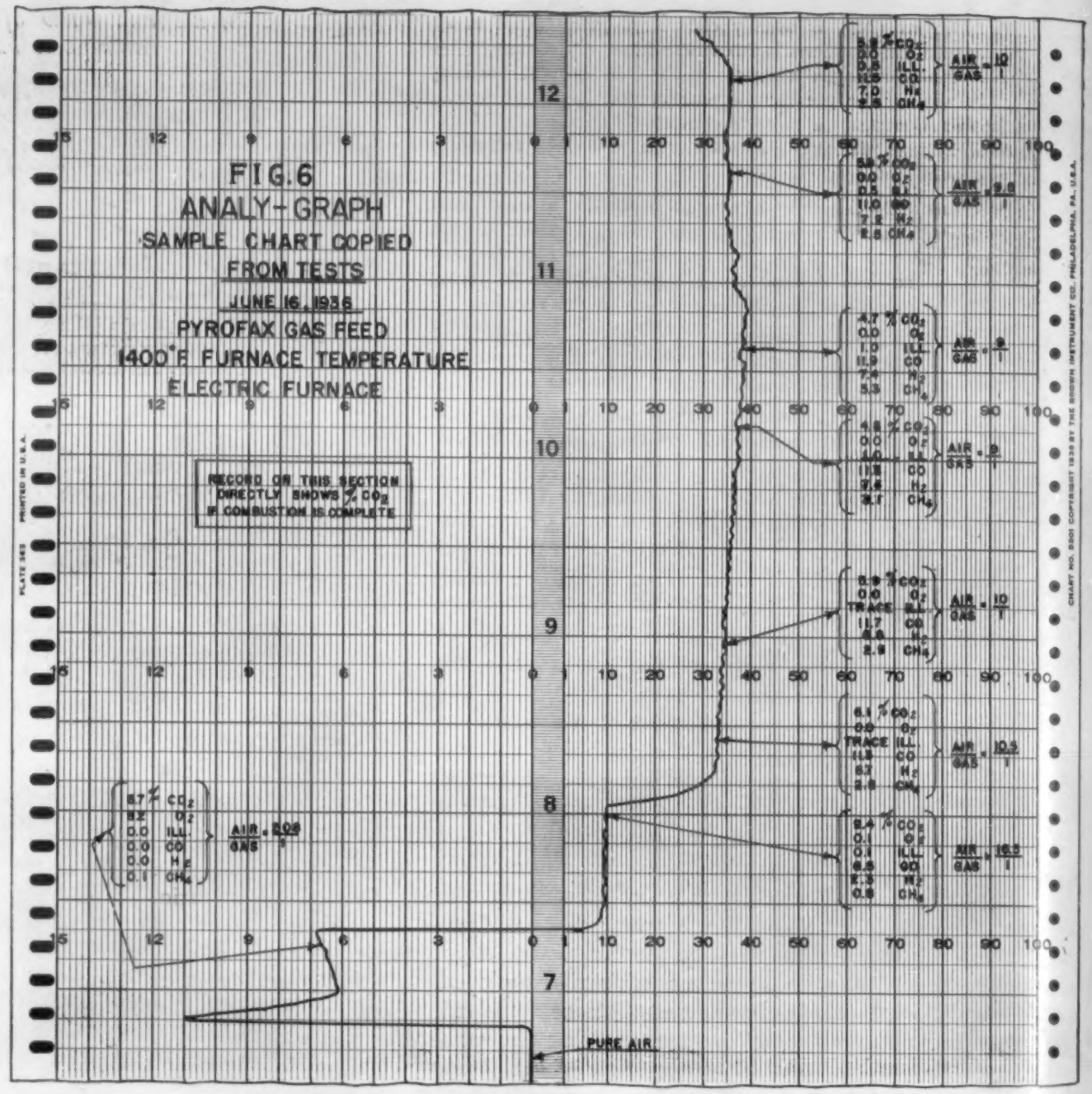


Fig. 6—Sample Chart from Thermal Conductivity Recorder Illustrating the Type of Data Secured during Test.

Fig. 5.—Curves Showing the Creeping Changes that Occur in Furnace Atmospheres After Valve Adjustments.

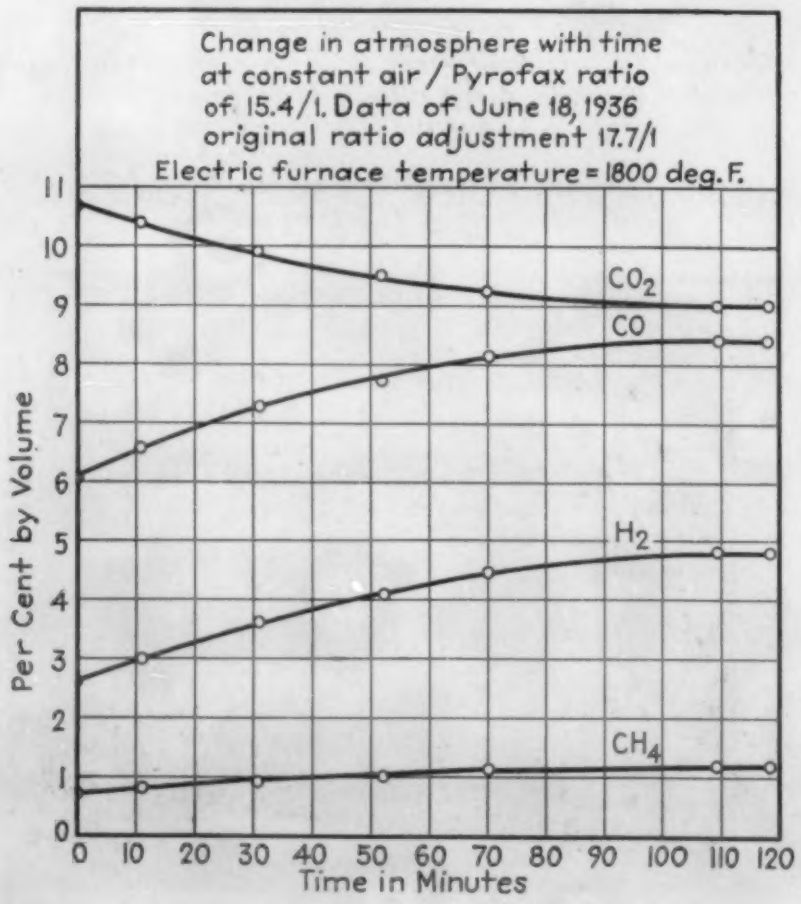


Fig. 2 shows a partial cross section of the electrically heated furnace used in the work. A pre-combustion chamber, not shown in the diagram, served to permit the gas and air to burn and reach relative stability before the mixture was admitted to the work chamber. The furnace was heated by current passing through Globar resistor elements mounted on each side of the work chamber. The combustion chamber temperature was measured by means of a thermocouple imbedded into the wall about ½ in. from the actual combustion space. The furnace temperature was measured in the usual manner.

All gas samples were secured through Sillimanite sampling tubes installed 3 in. inside each furnace and about 2 in. above the hearth. This, it was reasoned, was the location in the furnace which should give the best representative sample of the gas that would actually surround work in the furnace.

The use of a Sillimanite or porcelain sampling tube was dictated by the known fact that nickel and iron each tend to react with the furnace gases, when hot, and would thus render results unreliable. In view of the fact that only relative values were required, we discarded the thought of using a water-cooled sampling tube. The results have justified this.

Two widely differing gases were used for the furnaces; i.e., "Pyrofax" and manufactured water gas. Pyrofax is approximately 99 per cent propane, while the other was Providence City Gas with an average analysis of 1.7 per cent CO_2; 0.5 per cent O_2; 10.0 per cent CO; 27.3 per

cent CH_4 (probably a portion of this was ethane); 42.7 per cent H_2; 15.1 per cent N_2; and 2.7 per cent illuminants. On the basis of work done by a number of other investigators, it was reasoned that these two gases differed sufficiently widely in characteristics so that investigation would give data which could be correctly interpreted to apply to other gases.

A gas sample was continuously drawn from the furnace under test by means of analysis equipment, such as shown in Fig. 3. The gas passed through a condenser, calcium chloride drier, and cellulose filter before analysis. This, of course, removed most of the water vapor in the atmosphere from consideration. After the filter, the sample was drawn through a thermal conductivity cell, an exit seal, and a water aspirator. At 20-min. intervals, a portion of the sample was manually drawn into a chemical 100 cc. Orsat (Fisher Scientific Co. Type "D" Analyzer) and volumetric tests were made for the constituents by the following means:

CO_2 by absorption in caustic potash solution.
O_2 by absorption in acid pyrogallate.
Illuminants by absorption in fuming sulphuric acid.
CO by absorption in acid cuprous chloride.
H_2 by combustion in a measured quantity of air.
CH_4 by absorption of CO_2 in caustic potash after burning of the sample.

Simultaneously with the drawing of the Orsat sample, readings of the air flow, gas flow, time, relative humidity, and thermal conductivity were made.

As a basic part of the investigation, it was decided to provide a record of the thermal conductivity of the gases. Thermal conductivity meters are based upon the ability of heat to flow through a gas mixture. Such meters usually take the form of a Wheatstone bridge, of which two or more arms are made from wire having a high temperature coefficient. Each of these arms or filaments is enclosed in a cellular space and current is passed through the bridge to heat the filaments. In one cell is sealed air, while the sample gas is passed through the other. As the composition of the gas sample changes, the relative temperature of the exposed filament changes—thus changing its resistance, and unbalancing the Wheatstone bridge. The amount of this unbalance may then be measured.

Anaylsis equipment for this purpose was, therefore, incorporated in the test and a graphic record produced on a potentiometer such as shown in Fig. 4. The instrument proved so useful during the tests and in subsequent production work that a device based on this principle and called the "Furnace Atmosphere Analy-Graph" resulted.

In Fig. 6 is shown a copy of a test chart transcribed upon the type of chart which is now being used on the Furnace Atmosphere Analy-Graph. This sample serves to illustrate the type of data secured. In this particular instance, the measurements were made on the electric furnace using Pyrofax gas feed with an operating furnace temperature of 1400 deg. F. The chart illustrates how the instrument was useful both for complete and incomplete combustion conditions.

Throughout the tests, care was taken that simultaneous readings were made and that relative equilibrium existed in the furnace. The importance of this will be appreciated in view of the time curves shown in Fig. 5, which illustrate the "creeping" of the furnace atmosphere after a change in the air/gas ratio (from 17.7/1 to 15.4/1) was made. Is it any wonder observers, like doctors, disagree?

(To be concluded)

LETTERS TO THE EDITOR

Cupola Duplexing for Electric Steel Castings

To the Editor: The article by Kinnear and Gillett in the December issue of METALS AND ALLOYS interests me greatly.

It so happens that duplexing cupola melted steel scrap to an electric furnace for making steel castings was proposed and greatly increased output at approximately equal cost with cold melting was pointed out in a paper[1] by the writer before the American Foundrymen's Association in 1912, where we refer you to page 245. Hot metal of 4 per cent C was taken down to 0.50 per cent C by oreing down in induction furnaces prior to 1909.[2]

When one of my electric furnaces was installed at the La Consolidada in Mexico City in 1922, on account of the guarantees made I went there to operate it. The scrap was about one-third cast, one-third malleable and the balance very rusty steel scrap with an occasional piece of wrought iron. We did not have the cupola but the carbon was in the mixture with a vengeance. We ored it down with roll scale and a little manganese ore. After a few trials we had no more boiling out at the doors. I have been in communication with these people ever since this was first started and, from what I gather, their scrap mixture is about the same today after these many years.

C. H. VOM BAUR, CONSULTING ENGINEER
Hartford Electric Steel Corp., Hartford, Conn.

[1] "The Practicability of the Induction Furnace for the Making of Steel Castings." A.F.A., Vol. 20, 1912, pages 237-253.

[2] Kjellen. *Transactions*, American Electrochemical Society, Vol. 15, 1909, page 203.

Damping

To the Editor: Your recent editorial note in METALS AND ALLOYS for December on "Damping" has prompted me to write you of some work we are doing at M.I.T. along this line.

Instead of using a measurement of the damping capacity as an indication of the plastic behavior of metals particularly under conditions of repeated loading, we are using it as an indication of structural changes brought about by mechanical and thermal treatment. In the field of age hardening, the results seem very promising and apparently the damping test supplies one more tool to be used in studying the beginning of the precipitation process. The method also seems to be a sensitive indicator of the recovery in metals which have been reheated after cold work.

Our experimental work is just beginning in this field, but comparative results of sufficient precision apparently can be obtained fairly simply and I feel that damping measurements will be very useful in supplementing our other metallographic methods.

J. T. NORTON, MASS. INST. OF TECH.
Cambridge, Mass.

Courtesy Aluminum Company of America

In the harbor at Charleston, S. C. is this light buoy with superstructure and lantern fabricated from aluminum alloys possessing exceptional resistance to attack from salt spray and marine atmosphere. Because of the lightness of aluminum construction it was possible to use a 25-ft. tower and a 375-mm. lantern in place of the standard 16-ft. tower and 200-mm. lantern.

Phosphorus As An Alloying Element

IN STEELS FOR USE AT ELEVATED TEMPERATURES

by H. C. Cross and D. E. Krause

Metallurgists, Battelle Memorial Institute, Columbus, Ohio.

THE EFFECT OF PHOSPHORUS as an alloying element in low carbon, low alloy steels was discussed, in relation to properties at room temperature and lower temperatures, in an earlier article.[1] Phosphorus has a specific effect on the properties of steels at elevated temperatures, though the fact is as yet rarely appreciated.

The available references to the effect of phosphorus in steels for high temperature services are few. One which bore on the high temperature tensile and yield strengths of phosphorus containing steels appeared in a discussion by Speller[2] of a paper presented before the A.S.T.M. in 1924. In this, Speller had shown that the tensile strength and yield point of lap-welded steam pipe containing 0.09 C, 0.43 Mn and 0.013 per cent P were raised by increasing the phosphorus content to about 0.10 per cent. This was accomplished with little change in ductility. Tensile tests made at temperatures from 600 to 1000 deg. F. showed the higher phosphorus steel to have the greater tensile strength over the entire temperature range.

Other references[3, 4, 5, 6] in the literature, while mentioning the uses of larger than normal percentages of phosphorus in cast steels, in cast iron and in scale-resisting steels—in the latter because of increased scale resistance—give no suggestion as to the advantageous use of phosphorus in producing high temperature strength and resistance to deformation.

Curiously, one of the first indications which suggested that phosphorous steels might possess such properties as would make them suitable and desirable for use at elevated temperatures made itself felt during preparation of some of the steels previously tested. With them it was observed that greater power was required in forging and a larger number of passes was necessary in hot rolling to definite gages. These effects were observed to increase in proportion as the phosphorus content of the steels was increased. Hence both short time tensile testing and creep testing of phosphorus-bearing steels were undertaken at elevated temperatures.

Ellis[10] observed that a phosphorus-bearing steel was likewise distinctly less forgeable than carbon steel of the same carbon content. From his recent work on the forging behavior of "Cor-Ten," "Man-Ten," "Sil-Ten" and three straight carbon steels he concluded that the forgeability of "Cor-Ten" is distinctly less than carbon steel of the same carbon content and that the substitution of almost 0.75 per cent Si, about 0.5 per cent Cu, about 1.00 per cent Cr and about 0.15 per cent P for about 2.5 per cent Fe in a steel containing approximately 0.1 per cent C reduces its forgeability at all temperatures up to about 1200 deg. C. (2190 deg. F.). In this connection Ellis suggested that the fineness of grain may have had an important bearing upon the behavior of the steel. The indications are, however, that part of the reduced forgeability of "Cor-Ten" may be traced to the phosphorus which is present.

In our work, steels were prepared from 15-lb. high frequency furnace melts that were treated with 0.10 per cent aluminum to effect grain refinement and which were subsequently forged and rolled to about $\frac{3}{4}$-in. rounds. Their chemical compositions, set forth in Table I, show the types of steels employed in these tests.

Short-Time Tension Tests at Elevated Temperatures

SEVERAL of the steels listed in Table I were employed for short-time tension tests at room temperature and at 750, 850 and 950 deg. F. They were tested after heating to 1800 deg. F. for $\frac{1}{2}$ hr. and air cooling, followed by reheating to 1250 deg. F. for 4 hrs. and air cooling. The data are shown in Table II and Fig. I. For comparison purposes data on a plain carbon steel KI[7, 8] with 0.17 C, 0.42 Mn, 0.012 P and 0.035 per cent S whose tensile properties were determined by a group of laboratories are also given. This steel was heat treated by air cooling from 1650 to 1700 deg. F. after holding 1 hr., and provided the best available steel for comparison both as regards composition and heat treatment. An examination of the data emphasizes the influence of phosphorus.

Before proceeding with high temperature properties, the room temperature properties would seem to demand some

attention, if for no other reason than to confirm results of past experiences with phosphorus in the simple low carbon steels. The rise in the tensile and yield strengths and the increase in the value of the yield ratio are marked as the phosphorus increases. Of equal interest, especially since phosphorus has received broad condemnation in the past as being particularly responsible for low toughness, is the fact that the Charpy impact values of steel No. 1679 with 0.17 per cent P and steel No. 1680 with 0.31 per cent P are high and identical and that the elongation and reduction of area values are reasonably alike and not much different from those for steel KI with only 0.012 per cent P.

Phosphorus a Tonic Rather Than a Poison

The implications are clear that in mild steels phosphorus may, as Sauveur[9] nicely phrased it, serve as a tonic rather than a poison. The gains derived from increased tensile and yield strengths through its use in moderate quantities can more than offset the slight decline in toughness or ductility.

This increased strength, brought about through alloying with phosphorus, holds at elevated temperatures. In Table II steels No. 877 and No. 1052, for example, show that an increase in phosphorus content increases the tensile strength and yield strength without lowering the ductility. This is more noticeable at 750 deg. 5. and at 850 deg. F. At 950 deg. F., although the higher phosphorus steel still manifests the best properties, the difference is no longer as great. Thus at 750 deg. F. the 0.35 per cent P steel No. 1052 as compared with the 0.21 per cent P steel No. 877 has a tensile strength which is 7000 lbs. per sq. in. greater and a yield strength which is 8000 lbs. per sq. in. greater. At 950 deg. F. these differences in the two properties are reduced to 2000 lbs. per sq. in. and 5000 lbs. per sq. in. respectively.

Data are not available for direct comparisons with the low phosphorus steel KI; nevertheless it is evident that the higher phosphorus steels have much the better properties at the temperatures mentioned. At 950 deg. F. the 0.21 per cent P steel No. 877 is superior in yield to steel KI at 800 deg. F. The respective tensile strengths under these conditions are somewhat in favor of steel KI but this might be offset by further alloying with phosphorus. Steel No. 1052 containing 0.35 per cent P as an example has the same tensile strength at 950 deg. F. as steel KI has at 800 deg. F.

An additional 1 per cent Cr in steel with 0.20 per cent P (steel No. 1053), while not improving the yield at room temperature but improving the tensile strength, produces better tensile and yield strengths at the elevated temperatures. The case is particularly noticeable at 850 and 950 deg. F. where substantial differences occur between properties of steel No. 877 and steel No. 1053. The spread widens at the higher temperatures indicating that the chromium additions are more effective with high phosphorus in the higher temperature bracket.

With these promising short-time high temperature tensile data at hand one naturally wonders whether this would be one of the cases where good resistance to deformation under sustained loads or creep resistance would accompany the good short-time tensile properties.

Table I.—Chemical Composition of Phosphorus Steels Used in the Short Time Tensile and Creep Tests

Heat No.	C %	Si %	Mn %	P %	S %	Cr %	Mo %	Cu %
877	0.073	0.11	0.37	0.21	0.043	...	...	...
1210	0.10*	0.20*	0.40*	0.02*	...	1.00*	0.20*	...
1211	0.10	0.20*	0.40*	0.50*	...	1.00*	...	...
1212	0.10	0.20*	0.40*	0.03*	...	1.00*	0.50*	...
1052	0.10*	0.10*	0.40*	0.35*	...	...	...	...
1053	0.10*	0.10*	0.40*	0.20*	...	1.00*	...	...
1679	0.12	0.10*	0.50*	0.17	...	...	...	...
1680	0.12	0.10*	0.50*	0.31	...	...	...	...
1703	0.13	0.10*	0.50*	0.18	...	0.94	...	...
1730	0.16	1.01	0.50*	0.18	0.04	...	...	1.00
1734	0.16	1.05	0.60	0.324	0.04	0.97	...	0.37
1747	0.17	0.10*	0.53	0.17	...	0.92	0.20	...
1750	0.18	0.12	0.54	0.17	...	2.38	0.21	...
1892	0.11	0.05	0.35	0.176	...	...	0.21	...

* Values marked with asterisks are intended values.

Long-Time Tension or Creep Tests at Elevated Temperatures

TO explore the possibilities of phosphorus bearing steels for high temperature creep service, initial studies were begun at 850 deg. F. and at 950 deg. F. with loads of

Table II.—Short-Time Tensile Properties of Phosphorus Steels.

Heat No.	Composition C	Composition P	Composition Cr	Temperature, deg. F.	Tensile Strength, lbs. per sq. in.	Yield Strength, lbs. per sq. in.(A)	Elongation in 2 in., per cent	Reduction of Area, per cent	Charpy Impact Resistance, ft. lbs.	Heat Treatment
KI	0.17	0.012	...	Room	55,500	30,000	40	67	..	(D)
KI	0.17	0.012	...	800	45,000	20,000	45	80	..	(D)
KI	0.17	0.012	...	1000	26,000	15,000	60	90	..	(D)
1679	0.12	0.17	...	Room	67,500	45,000	33	67	37	(B)
877-5	0.07	0.21	...	750	68,800	26,600	43	70	..	(C)
877-3	0.07	0.21	...	850	56,750	25,700	40	76	..	(C)
877-4	0.07	0.21	...	950	42,750	22,200	60	87	..	(C)
1680	0.12	0.31	...	Room	79,500	56,000	34	62	37	(E)
1052-4	0.10	0.35	...	750	76,500	34,400	38	63	..	(C)
1052-3	0.10	0.35	...	850	63,350	33,400	59	76	..	(C)
1052-5	0.10	0.35	...	950	44,900	27,000	65	84	..	(C)
1703	0.13	0.18	0.94	Room	75,200	45,500	36	69	39	(F)
1053-3	0.10	0.20	1.00	750	69,750	28,500	35	70	..	(C)
1053-4	0.10	0.20	1.00	850	63,250	28,400	41	78	..	(C)
1053-5	0.10	0.20	1.00	950	48,400	27,500	50	85	..	(C)

A—Yield strength taken as stress to produce permanent set of 0.2 per cent.
B—1725 deg. F.—½ hr.—air cooled.
C—1800 deg. F.—½ hr.—air cooled—1250 deg. F.—4 hrs.—air cooled.
D—1650 to 1700 deg. F.—1 hr.—air cooled.
E—1800 deg. F.—½ hr.—air cooled.
F—1725 deg. F.—½ hr.—air cooled.

Procedure of test was according to A.S.T.M. Specification E21-34T.

12,000 lbs. per sq. in. employing steels Nos. 877, 1052, 1053, 1210, 1211 and 1212 whose compositions are shown in Table I. The studies later embraced the more highly alloyed steels Nos. 1730, 1734, 1747, 1750 and 1892 not only at the above temperatures and loadings but also at higher loadings. Table III summarizes the creep properties which were obtained.

The time-deformation curves for steels Nos. 877, 1052, 1053, 1210, 1211 and 1212 are shown in Fig. 2, those for steels Nos. 1747 and 1892 are shown in Fig. 3, and those for steels Nos. 1730, 1734, and 1750 are shown in Fig. 4.

First consideration might be given to the creep properties of the same steels used in the short-time tension tests. All were tested at a load of 12,000 lbs. per sq. in, at 850 deg. F. The detailed results of the tests in Table III and the time-deformation curves appearing in Fig. 2 show the marked effect in steels Nos. 877 and 1052 of the increase of the phosphorus content from 0.21 to 0.35 per cent. After a short initial period of decreasing rate of deformation (about 100 hrs.) steel No. 1052 with 0.35 per cent P deformed at a rate considerably slower than steel No. 877 with 0.21 per cent P. With both steels the rate of deformation decreased steadily over the first 800 hrs. Comparing the two steels at the 1000-hr. period, the 0.21 per cent P steel showed a rate of 0.000074 per cent per hr. while the 0.35 per cent P steel showed a rate of only 0.00001 per cent per hour. Increasing strain-hardening resulted in a further reduction of the rate for the 0.21 per cent P steel to 0.00004 per cent per hr. at 1500 hours.

An index of the total deformation for these two steels after 10,000 hrs. can be secured by extrapolating the time-deformation curves using the final rate of deformation when the tests were discontinued. This gives a calculated total deformation of 0.865 per cent for steel No. 877 with 0.21 per cent P and 0.22 per cent for steel No. 1052 with 0.35 per cent P.

These data clearly indicate the beneficial effect of phosphorus when compared with data for a normalized 0.17

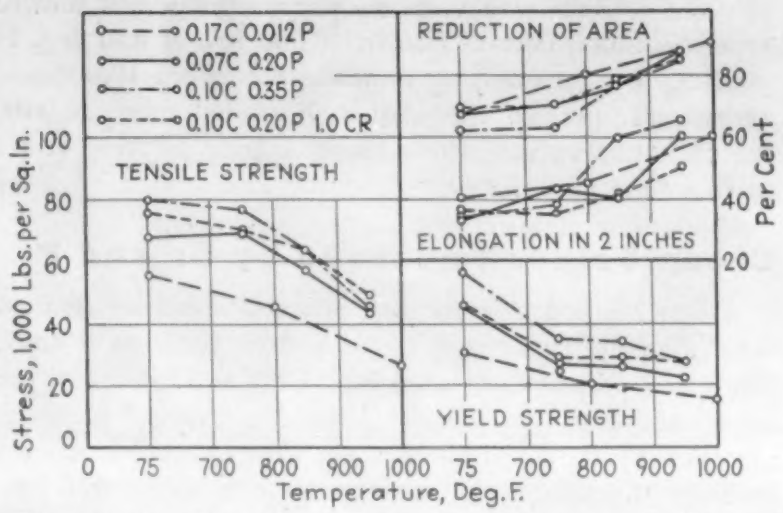


Fig. 1. Tension Test Data at Ordinary and Elevated Temperatures for Steels Containing 0.012, 0.20 and 0.35 Per Cent Phosphorus.

Fig. 2. Time-Deformation Curves at 850 and 950 Deg. F. for Steels Nos. 877, 1052, 1053, 1210, 1211 and 1212. For their detailed chemical composition, see Table I.

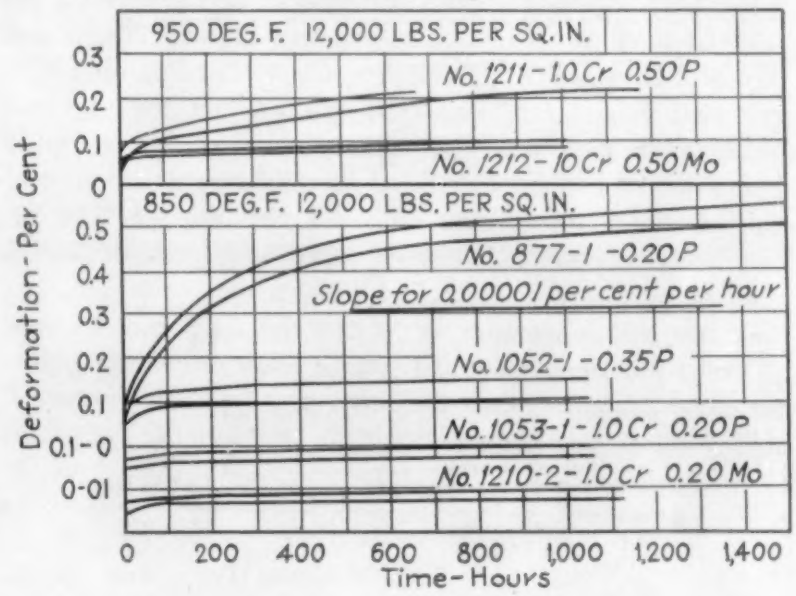

950 DEG. F. 12,000 LBS. PER SQ. IN.
No. 1211 - 1.0 Cr 0.50 P
No. 1212 - 1.0 Cr 0.50 Mo
850 DEG. F. 12,000 LBS. PER SQ. IN.
No. 877 - 1 - 0.20 P
Slope for 0.00001 per cent per hour
No. 1052 - 1 - 0.35 P
No. 1053 - 1 - 1.0 Cr 0.20 P
No. 1210 - 2 - 1.0 Cr 0.20 Mo
Deformation - Per Cent
Time - Hours

Table III.—Creep Test Data for Phosphorus, Chromium-Phosphorous, Chromium-Molybdenum and Chromium-Phosphorus-Molybdenum Steels.

Specimen No.	Readings Taken at	Temperature of Test, deg. F.	Load, lbs. per sq. in.	Duration of Test, hrs.	Initial Deformation, per cent	At 1000 Hrs. Rate of Deformation, per cent per hr.	At 1000 Hrs. Total Deformation, per cent	Total Deformation at 10,000 hrs.	Chemical Composition—Per Cent C	Cr	P	Mo	Si	Remarks
877-1	Front	850	12000	1510	0.035	0.000074	0.48	0.865	0.07	...	0.21	...	...	Rate 0.00004% per hr. at 1500 hrs.
877-1	Back	850	12000	1510	0.069	0.000074	0.525	....	0.07	...	0.21	...	...	
1052-1	Front	850	12000	1050	0.063	0.00001	0.15	0.22	0.10	...	0.35	...	...	
1052-1	Back	850	12000	1050	0.043	0.00001	0.11	....	0.10	...	0.35	...	...	
1053-1	Front	850	12000	1060	0.046	0.00001	0.075	0.18	0.10	1.0	0.20	...	...	
1053-1	Back	850	12000	1060	0.066	0.00001	0.102	....	0.10	1.0	0.20	...	...	
1210-2	Front	850	12000	1130	0.042	0.00001	0.092	0.167	0.10	1.0	...	0.20	...	
1210-2	Back	850	12000	1130	0.067	0.00001	0.075	....	0.10	1.0	...	0.20	...	
1211	Front	950	12000	1175	0.032	0.00005	0.112	0.674	0.10	1.0	0.50	...	...	
1211	Back	950	12000	1175	0.079			....	0.10	1.0	0.50	...	...	
1212	Front	950	12000	1010	0.062	0.00001	0.098	0.18	0.10	1.0	0.03	0.50	...	
1212	Back	950	12000	1010	0.055	0.00001	0.083	....	0.10	1.0	0.03	0.50	...	
1730	Front	850	20000	210	0.105	0.0122	2.972	over	0.16	...	0.18	...	1.0	1.0% Cu—discontinued at 210 hrs.
1730	Back	850	20000	210	0.114	0.0122	3.005	0.125	0.16	...	0.18	...	...	
1892	Front	950	12000	1175	0.064	0.000075	0.225	0.904	0.11	...	0.17	0.21	...	
1892	Back	950	12000	1175	0.070	0.000075	0.236	....	0.11	...	0.17	0.21	...	
1747	Front	950	12000	1410	0.067	0.00001 to	0.130	0.236	0.17	0.92	0.17	0.20	...	
1747	Back	950	12000	1410	0.052	0.000015	0.103	....	0.17	0.92	0.17	0.20	...	
1734	Front	850	20000	1375	0.070	0.000055	0.170	0.697	0.16	0.97	0.32	...	1.05	0.37% Cu
1734	Back	850	20000	1375	0.132	0.000055	0.248	....	0.16	0.97	0.32	...	1.05	
1750	Front	850	20000	1375	0.081	0.000010	0.144	0.213	0.18	2.38	0.17	0.21	...	
1750	Back	850	20000	1375	0.120	0.000010	0.100	....	0.18	2.38	0.17	0.21	...	
1750	Front	850	28000	1685	0.122	0.000015	0.187	0.327	0.18	2.38	0.17	0.21	...	
1750	Back	850	28000	1685	0.142	0.000015	0.206	....	0.18	2.38	0.17	0.21	...	
1747(a)	Front	950	12000	1488	0.064	0.000095	0.220	1.068	0.17	0.92	0.17	0.20	...	
1747(a)	Back	950	12000	1488	0.052	0.000095	0.206	....	0.17	0.92	0.17	0.20	...	
1734(a)	Front	850	20000	1488	0.075	0.000085	0.230	1.018	0.12	0.97	0.27	...	1.05	0.37% Cu
1734(a)	Back	850	20000	1488	0.117	0.000085	0.287	....	0.12	0.97	0.27	...	1.05	
1750(a)	Front	850	28000	1488	0.151	0.000025	0.213	0.413	0.14	2.38	0.17	0.21	...	
1750(a)	Back	850	28000	1488	0.110	0.000025	0.163	....	0.14	2.38	0.17	0.21	...	

Note: Specimens tested as normalized and drawn except as indicated. (a)—Oil quenched and drawn.

per cent C steel[8] with very low phosphorus which showed 1 per cent total deformation in 10,000 hrs. at 850 deg. F. produced by a stress lying somewhere between 10,000 and 11,000 lbs. per sq. in. Although loaded more heavily, the phosphorus steels showed a lower rate of creep and a smaller total deformation.

Creep Values Improved by Cr and P

A very marked improvement in creep resistance resulted from alloying 1 per cent Cr to a 0.20 per cent P steel. The creep properties of steel No. 1053 at 12,000 lbs. per sq. in. and 850 deg. F. showed that the creep resistance is increased by the addition of 1 per cent Cr until this steel becomes comparable in creep properties with steel No. 1052 having 0.35 per cent P but no chromium. The Cr-P combination is an effective one.

Similar long-time tension tests were made to give an indication of the relative effects of phosphorus and molybdenum in imparting creep resistance at elevated temperatures as well as of the possibility of substituting phosphorus for a portion of the molybdenum sometimes used. These additional tests permitted a comparison between two 1 per cent Cr steels containing 0.20 per cent P and 0.20 per cent Mo and between two 1 per cent Cr steels containing 0.50 per cent P and 0.50 per cent Mo. Other tests on two steels, both with 0.20 per cent Mo and 0.17 per cent P but with 1 per cent Cr added to only one of them, permitted direct comparisons with a 1 per cent Cr, 0.50 per cent Mo steel as to the effect of substituting phosphorus for molybdenum in steel with and without the chromium.

It was somewhat unexpected that the 1 per cent Cr 0.20 per cent Mo steel No. 1210 should show only slightly better creep properties than the 1 per cent Cr 0.20 per cent P steel No. 1053. The difference in rates for the two steels is very small and since their total deformations are about equal, for all practical purposes at 850 deg. F. and 12,000 lbs. per sq. in., the steels may be considered to possess comparable creep resistance.

Steel No. 1211 with 1 per cent Cr and 0.50 per cent P and steel No. 1212 with 1 per cent Cr and 0.50 per cent Mo were expected to show better creep resistance than the other steels. For that reason they were tested at the same load of 12,000 lbs. per sq. in. but at the higher temperature of 950 deg. F.

The creep rate of steel No. 1211 at 1000 hrs. was about 0.00005 per cent per hr. This was five times the rate for steel No. 1212. But as the rate for steel No. 1211 was steadily decreasing as the test progressed, the continued strain-hardening of this steel should ultimately lead to a very low rate of creep. Under these conditions it is natural that the total deformation in 10,000 hrs, for the molybdenum steel should have been smaller than it was for the phosphorus steel.

Effect of P Compared With That of Mo

While, from the standpoint of creep resistance, the benefits of phosphorus in steel when employed alone or with chromium were definitely established, it remained to evaluate the effect of combining phosphorus with other well known strengthening alloying elements. In this regard various combinations of phosphorus and molybdenum were selected and the creep resistance of steels containing these elements compared.

Steel No. 1747 contained 0.92 Cr, 0.17 P, and 0.20 per cent Mo; steel No. 1892 contained 0.17 P, 0.21 per cent Mo and no chromium. These two steels when tested at 950 deg. F. and 12,000 lbs. per sq. in. for a period extend-

Table IV.—Room Temperature Tensile and Impact Properties of Phosphorus Steels.

Heat No.	C %	P %	Cr %	Cu %	Si %	Mo %	Mn %	Tensile Strength, lbs. per sq. in.	Yield Strength, lbs. per sq. in.	Elongation in 2 in., per cent	Reduction of Area, per cent	Charpy Impact, ft. lbs.
1892(A)	0.11	0.18	...	...	0.05	0.21	0.50	81,500	46,000	33	65	36
1747(B)	0.17	0.17	0.92	...	0.10	0.20	0.53	79,000	51,500	31	69	41
1747(D)	0.17	0.17	0.92	...	0.10	0.20	0.53	101,000	80,000	25	68	38
1730(A)	0.16	0.18	...	1.00	1.01	...	0.50	88,500	66,000	32	60	22
1734(C)	0.12	0.32	0.97	0.37	1.05	...	0.60	102,000	71,500	31	64	29
1734(E)	0.16	0.32	0.97	0.37	1.05	...	0.60	100,000	80,000	30	62	21
1750(B)	0.18	0.17	2.38	...	0.12	0.21	0.54	95,000	68,000	26	70	40
1750(D)	0.14	0.17	2.38	...	0.12	0.21	0.54	108,500	91,500	23	66	27

A—Normalized ½ hr. at 1725 deg. F.—air cooled.
B—Normalized 1 hr. at 1700 deg. F.—air cooled—1250 deg. F.—1 hr.—air cooled.
C—Normalized ½ hr. at 1550 deg. F.—air cooled.
D—Heated 1 hr. at 1700 deg. F.—oil quenched—1100 deg. F.—1 hr.—air cooled.
E—Heated ½ hr. at 1550 deg. F.—oil quenched—1100 deg. F.—1 hr.—air cooled.

Table V.—Impact Properties of Phosphorus Steels As Heat Treated and After Creep Test

Heat No.	C %	Mn %	P %	Cr %	Cu %	Si %	Mo %	Charpy(A) Impact Resistance as Heat-Treated, ft. lbs.	Time in Creep Test, Hrs.		Izod Impact Resistance,(B) Ft. Lbs.	
									850 deg. F.	950 deg. F.	As Heat Treated	After Creep Test
877	0.07	0.37	0.21	...	...	0.11	...	37(C)	1510	....	20, 26	46, 2.5
1052	0.10	0.40	0.35	...	...	0.10	...	23(C)	1050	....	3.5, 2.5	4.5, 2.5
1053	0.10	0.40	0.20	1.00	...	0.10	...	39, 37(C)	1060	....	64, 97	75, 53
1210	0.10	0.40	...	1.00	...	0.20	0.20	42, 41(C)	1130	....	.....	over 110
1211	0.10	0.40	0.50	1.00	...	0.20	...		....	1175	.....	4.0, 2.0
1212	0.10	0.40	...	1.00	...	0.20	0.50	59, 57(C)	....	1010	.....	over 110
1892	0.11	0.35	0.18	...	...	0.05	0.21	41, 40(D)	....	1224	.....	88, 91
1747	0.17	0.53	0.17	0.92	...	...	0.20	42, 41(D)	....	1469	.....	72, 79
1747	0.17	0.53	0.17	0.92	...	...	0.20	40, 36(F)	....	1488	.....	36, 51
1734	0.16	0.60	0.32	0.97	0.37	1.05	...	21, 22(E)	1375	....	.....	7.0, 13.5
1734	0.12	0.60	0.27	0.97	0.37	1.05	...	21, 21(F)	1488	....	.....	6.5, 7.9
1750	0.18	0.54	0.17	2.38	...	0.12	0.21	30, 35(E)	1375	....	.....	26, 18
1750	0.14	0.54	0.17	2.38	...	0.12	0.21	31, 25(F)	1488	....	.....	19, 17

A—Charpy keyhole notch specimen.
B—Standard round Izod impact test specimen—"V" notch.
C—Tested as normalized without drawing.
D—Drawn at 1250 deg. F.
E—Normalized and drawn at 1100 deg. F.
F—Oil quenched and drawn at 1100 deg. F.

ing over 1000 hrs. showed rates of creep which differed by a factor of five, the difference being accounted for by the absence of chromium in steel No. 1892. Their time-deformation curves may be found in Fig. 3.

The important function of chromium in steels for high temperatures was again demonstrated by these tests. They indicated that molybdenum and particularly phosphorus exert a greater influence upon creep properties when chromium is present. They also demonstrated the important and interesting effect of phosphorus. The creep rate of steel No. 1747 at 950 deg. F. and 12,000 lbs. per sq. in. was almost identical to the rate of creep of steel No. 1212 which contained only a nominal quantity of phosphorus, 1 per cent Cr and 0.50 per cent Mo. The low molybdenum in conjunction with phosphorus in steel No. 1747 was therefore almost equally as effective toward imparting creep resistance as the 0.50 per cent Mo was in steel No. 1212. The total deformation of the latter steel was, however, somewhat less.

P Acts Much Like W and Mo

Without the implications of an established generalization, since it is dangerous to evaluate the effect of phosphorus solely from tests of this nature, it would appear that phosphorus acts much like tungsten and molybdenum in bestowing creep resistance to steel and that phosphorus has the apparent ability to replace at least a portion of the more expensive molybdenum in some steels for high temperature service without materially affecting the creep properties.

During the investigation on phosphorus as an alloying element in steels, a large number of heats were made using varying alloying combinations to which phosphorus was added. Several of these steels were tested in creep at 850 deg. F. with the thought that they might possess good creep resistance along with desirable room temperature tensile properties which would make them suitable as low cost materials for bolting service at elevated temperatures. The room temperature properties of three of such steels, along with properties of steels Nos. 1892 and 1747, are given in Table IV. The creep test data at 850 deg F. may be found in Table III and Fig. 4.

Creep testing was done at a load of 20,000 lbs. per sq. in. Steel No. 1730 with 1.00 Cu, 1.01 Si and 0.18 per cent P showed the very rapid rate of deformation of about 0.0122 per cent per hr. and its testing was therefore discontinued after 210 hrs. Of the other two steels, steel No. 1734 showed the greater rate of deformation. The creep rate of steel No. 1750 at a load of 20,000 lbs. per sq. in. was about equal to the rate for steel No. 1747 at 12,000 lbs. per sq. in. The principal difference between the latter steels was their chromium content so that one can attribute the better creep resistance of steel No. 1750 to its higher chromium content.

Without the chromium the creep properties of the phosphorus-copper-silicon steel were poor. The copper and silicon appeared to be of no definite help as such but, along with chromium, a phosphorus-bearing steel of good creep resistance was obtained.

A final test was made on steel No. 1750 at a load of 28,000 lbs. per sq. in. at 850 deg. F., which showed a rate of creep and total deformation slightly higher than for that obtained at 20,000 lbs. per sq. in.

In an effort to develop, in several of the steels, higher

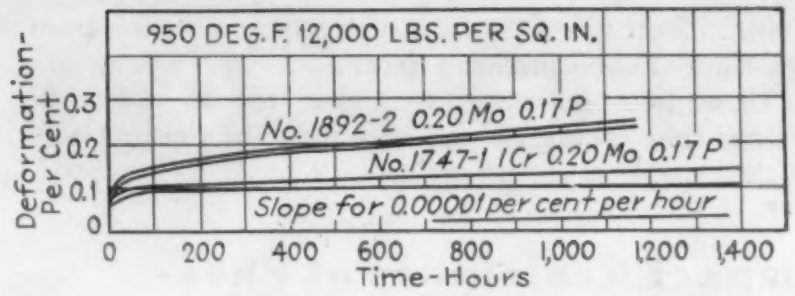


Fig. 3. Time-Deformation Curves at 950 Deg. F. for Steels Nos. 1892 and 1747. For their detailed chemical Composition, see Table I.

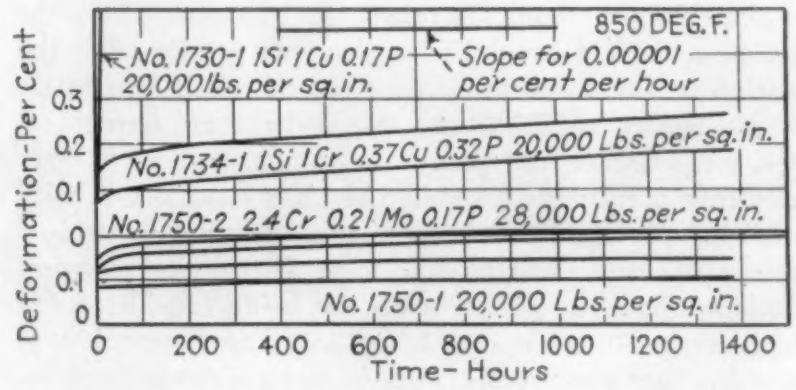


Fig. 4. Time-Deformation Curves at 850 Deg. F. for Steels Nos. 1730, 1734 and 1750. For their detailed chemical composition, see Table 1.

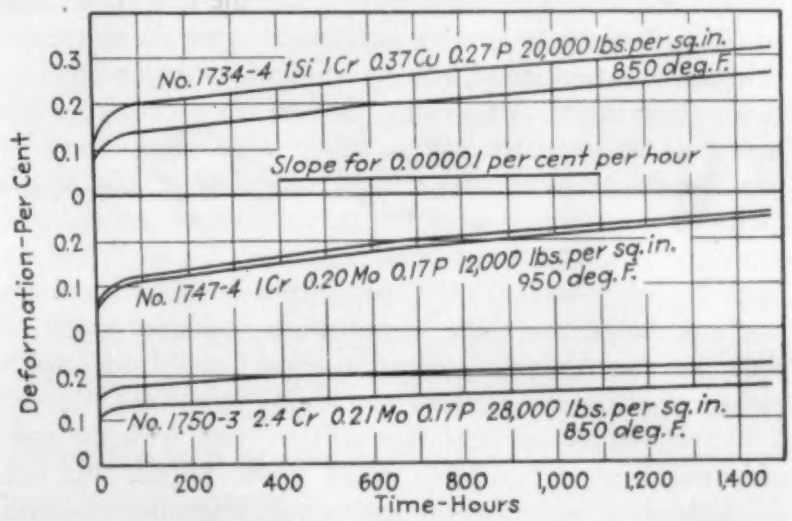


Fig. 5. Time-Deformation Curves at 850 Deg. F. for Steels Nos. 1734 and 1750 and at 950 Deg. F. for Steel No. 1747. (Tested as oil quenched and drawn.) For their detailed chemical composition, see Table 1.

yield and tensile strengths which would make them more suitable for bolting service, tests were made on steels Nos. 1747, 1734, and 1750 as oil quenched and drawn. The room temperature properties obtained are shown in Table IV, and the creep test data in Table III and Fig. 5.

In steels No. 1747 and 1750 considerably higher tensile strengths were obtained from oil quenching and drawing as compared with the properties as normalized and drawn (see Table IV). The yield strengths were also increased appreciably; steels Nos. 1747 and 1750 showing greater effects from the different heat treatment than steel No. 1734. Ductility and impact valves showed no significant change.

In the creep tests, all three steels show higher creep rates as oil quenched and drawn than when normalized and

drawn. Steel No. 1750 most nearly approaches the creep resistance as normalized and drawn.

These tests indicate that higher tensile and yield strengths are obtained by oil quenching and drawing only at the expense of creep resistance.

Impact Resistance of Phosphorus Steels As Heat Treated and After Testing for Creep

IN former publications[1, 3] it was shown that, in steel of suitably low carbon content, an increase of phosphorus, within definite limits, increases the hardness, raises the tensile and yield strengths but does not greatly affect the static ductility. For many purposes the steels still retain a satisfactory toughness as shown by their impact resistance. Use of phosphorus in combination with other elements, particularly chromium and to a lesser degree with nickel, copper and molybdenum tends to produce steel of somewhat better toughness. These factors are very important when phosphorus steels are being considered for high temperature service. In no other field, probably, is a satisfactory room temperature impact resistance more insistently demanded than in the field where steels are intermittently used at elevated temperatures and are liable to be subjected to shock during shut downs. The data previously presented have indicated that the room temperature toughness of steels not too highly alloyed with phosphorus is satisfactory for most purposes. It still remains to show that the toughness is retained after the steels are subjected to prolonged heating at service temperatures.

To some extent this information can be gained from impact tests on steels used in the creep tests. For determining the impact resistance, round Izod impact test specimens were machined from the 0.505-in. diameter reduced section of the creep test specimens. In Table V are set forth the composition, the Charpy impact resistance of the steels as heat-treated, the temperature and the length of time the steels were at temperature and the Izod impact resistance of the steels after creep testing.

In the heat-treated condition all the steels, with the possible exception of steel No. 1211 whose impact was not determined, possessed a Charpy impact resistance of more than 20 ft. lbs. Steel No. 1052 is unusual in this regard for normally a 0.35 per cent P steel is brittle in impact. Izod tests on the same steel after creep testing showed it to be brittle.

The impact values of the steels, with the exception of steels Nos. 1052 and 1211, were still good after creep testing. Steel No. 877 had one low and one high impact value. This erratic nature of the impact is not an unusual occurrence among the "border-line" alloys, i.e., alloys containing 0.25 to 0.35 per cent P, though it appears to be absent in steels with less than 0.20 per cent P.

Steels Nos. 1210 and 1212 with the lowest phosphorus contents have the highest notch toughness. The natural consequence of alloying with phosphorus is to lower the impact, yet most of the phosphorus bearing steels, tested in creep, possess impact values above 40 ft. lbs. which is more than adequate to meet ordinary requirements.

These impact tests indicated that, for service at elevated temperatures where it is important to maintain a satisfactory impact toughness, the phosphorus content of the steel can be substantial but not much above 0.20 per cent unless it is augmented by other alloying elements such as chromium, copper and molybdenum, in which case somewhat more phosphorus can be tolerated. Where impact resistance or toughness are of no importance then, of course, larger quantities of phosphorus can profitably be employed.

Summary

PHOSPHORUS raises the tensile strength and yield strength of 0.10 to 0.17 per cent carbon steel at temperatures of 750, 850 and 950 deg. F. with little change in static ductility.

Phosphorus likewise produces better resistance to deformation under sustained load at elevated temperatures as determined by long-time tension or creep tests.

Phosphorus exerts a greater influence on the creep resistance in the presence of chromium.

Phosphorus acts much like tungsten and molybdenum in imparting greater tensile and yield strengths and resistance to deformation under sustained loads at elevated temperatures and there are indications that phosphorus might economically be used to substitute partly for some molybdenum commonly used.

When used in various combinations with chromium, molybdenum, copper, silicon and manganese with carbon contents up to about 0.18 per cent, phosphorus additions show promise in producing low cost steels suitable for bolting stock used at elevated temperatures.

When used in proper alloy combinations, steels to which phosphorus has been added show a satisfactory notch toughness as heat treated and also after exposure to temperature in the creep test.

Acknowledgment

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METALS AND ALLOYS IN THE

Printing Industry—II

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This is the second installment of a series of four on this subject. Part I was published in the January issue. The discussion is another in the series of articles on the general topic of the Metallurgical Needs of the Non-Metallurgical Industries.—Editor.

TYPE METALS

THE lead-tin-antimony alloys were used for type metals from the earliest beginnings of printing and virtually the same alloys have remained in use to this day. This is because they have several outstanding advantages, among these being low-melting point, good castability (running easily when molten and filling out the mold well), ready variation in hardness, and cheapness. It was formerly thought that the reason type metals filled out the mold so well was because they expanded on solidification. This has now been shown to be untrue, the type metals actually contracting on solidification.[1] However, the amount of contraction is considerably less than with other alloys.

The table shows the approximate compositions of the type metals. Electrotype metal which is merely used for backing up the electrotype shell, as will be described later, is the softest of the type metals. Linotype is next. As has been stated this is seldom used for direct printing, matter set in linotype slugs being usually duplicated. The size of the linotype slug permits the use of a weaker alloy but demands easy and rapid solidification, such as is obtainable in an eutectic alloy. Linotype metal is approximately at the composition of the ternary lead-antimony-tin eutectic. Stereotype and monotype metal are harder, and foundry metal is the hardest of the type metal alloys.

The compositions of the alloys shown in the table are only approximate and may be varied considerably, although the several classes indicated are usually kept separate. On the other hand, attempts have been made to use the same "universal metal" for both the linotype and monotype casting machines. The Government Printing Office has been doing this for over a year, using the same 6 per cent tin and 12 per cent antimony alloy in its linotype and monotype machines. The advantage of such a system is, of course, the convenience of remelting and adjusting only one metal composition instead of two. The question is whether this simplification in metal handling is sufficient to outweigh possible disadvantage attending the somewhat higher operating temperatures required for the linotype machine, and the somewhat softer type obtained from the monotype machine.

Table of Approximate Compositions of the Type Metals, Lead Base.

	Tin, Per cent	Anti-mony, Per cent	Melting Point Deg. C.	Deg. F.	Brinell Hardness
Electrotype	3	3	298	570	14
Linotype	4	12	246	475	22
Stereotype	6	14	260	500	24
Monotype	8	16	268	515	26
Foundry	14	24	318	605	32

The Zinc-Aluminum Alloys

The advantages of the lead-antimony-tin type metal alloys will be well illustrated by discussing another series of alloys, namely the zinc-aluminum alloys.

While the hardness and ductility of the type metal alloys are on the whole very satisfactory, they leave something to be desired for certain purposes. In stereotyping, for example, a considerably stronger, harder, and at the same time more ductile alloy than can possibly be obtained from ordinary type metal alloys, would be a decided improvement. The use of the zinc-aluminum alloys has therefore been suggested.[3] These are alloys of zinc with about 6 per cent aluminum. About 1 per cent copper may also be added.

Such alloys have about four to five times the hardness of ordinary stereotype metal and are at the same time tougher and more ductile. Their melting point, about 725 deg. F., is about 225 deg. F. higher than that of stereotype metal.

Although stereotype paper mats can be made to withstand the casting temperature of about 835 deg. F. required with the zinc-aluminum alloys, there are also other difficulties. The contraction of these alloys on solidification

The Main Casting Room of the American Type Founders Co., in Which is Cast Foundry Type Made from Special Formulas of Lead, Antimony, Tin and Copper. This room contains 202 automatic type-casting machines, each of which is capable of casting 14,000 individual pieces of small size type (6 point or 0.083 in.), or 1,800 pieces of large size, such as 72 point or inch high type. The long racks in the foreground contain type from the machine before being packed as fonts.

and on cooling to room temperature is considerably greater than for the ordinary type metals. The zinc-aluminum alloys do not have sufficient fluidity in the molten state to fill the mold or reproduce fine detail and they tend to crack when cast in thin and irregular shapes, probably due to their greater shrinkage. Efforts are still being made to overcome these difficulties, but the use of the zinc-aluminum alloys has not as yet become practical.

An aluminum-silicon alloy containing about 95 per cent aluminum and 5 per cent silicon, generally "modified" to give better casting properties, is used to a very limited extent to make so-called aluminotype printing plates. The melting point of these alloys, about 1,200 deg. F., is too high for casting into paper mats so the mold is made of plaster of Paris. The alloy is not affected by the chemicals in colored inks, and the plates may be made either curved or flat for reproducing type matter or the coarser halftones. Because of the lightness of these plates they are used for shipping advertising plates, etc., especially to foreign countries, to save postage.

Impurities, Dross and Casting Properties of Pb-Sb-Sn Type Metals

Certain impurities in type metals are quite detrimental, but this is so well known that ample precautions are generally taken to avoid such contamination, and troubles from the source are rare. Copper in amounts as low as 0.1 per cent is harmful because it combines with tin to form long needle-like crystals of high melting point and thus decreases the castability and tends to clog up the orifices in automatic type casting machines. Zinc in amounts as low as 0.1 per cent is extremely harmful by spoiling the castability and giving a granular metal. Aluminum has a similar effect. For these reasons strict precautions should be taken not to allow copper, brass, zinc, or aluminum in any form to get into lead-base type metals.

Arsenic is also considered to have an injurious effect. However, arsenic in amounts up to 0.15 per cent or more apparently does no harm to the type itself and up to 0.75 per cent has been used to improve the castability and hardness. Arsenic has been suspected, however, of having a corroding effect on the nozzles of type casting machines. Arsenic volatilizes readily so that the amount of arsenic in any batch of type metal rapidly decreases. Since cadmium has properties so similar to zinc, one would expect that cadmium would also have a harmful effect in type metals. On the contrary, cadmium appears to have a good effect, and the addition of about 0.5 per cent of cadmium to type metals has been suggested to lower the melting point and increase the castability.[6]

Dross is another form of impurity. To what extent type metal dross may remain behind in the melted metal, either

in solution in the bath or as entrapped fine particles, instead of floating up to the top, has not been determined. Apparently, contamination by dross is not a frequent cause of trouble. Fluxes, such as ammonium chloride or palm oil, may be used to deoxidize the bath and other deoxidizers might be useful.

A more frequent difficulty from drossing is the impoverishment of the bath in antimony and tin. These metals probably do not become oxidized more rapidly than lead, but since they are lighter or form a compound with each other which is lighter, they tend to rise to the top where they can be oxidized in greater proportion than the average concentration of the bath. This tendency to concentrate at the top also permits an abnormal percentage of metallic tin and antimony to be removed with the dross. To avoid undue drossing and particularly antimony and tin losses, the temperature of the melting pots should be kept as low as possible. The largest drossing losses occur in the melting pots rather than in the type casting machines where the temperature is more closely controlled and the metal is better protected from the air. Electric or gas immersion heaters and well insulated pots are a great aid in giving uniform, closely controlled heating and a minimum of dross. The use of a non-oxidizing atmosphere over melting pots logically offers a means of eliminating dross. In many plants the bath is stirred by bubbling compressed air through the molten metal. A non-oxidizing gas may also be used for this purpose.

The ability of the type metals to fill out fine detail in the mold may be referred to as castability. Exactly why the type metal alloys have such good castability is not very clearly understood. The low melting point and the relatively small contraction on solidification are probably the main causes.

It has also been suggested that the low surface tension of the type metals accounts for their good castability. Surface tension is the force which tends to break up a falling liquid stream into drops. Thus it has been held that the force which keeps a drop of molten metal spherical also opposes its entering a fine depression or opening in a mold. Of course, surface tension would only have an appreciable effect when the opening in the mold is very fine—indeed, of capillary or hair-fine dimensions. A force opposing surface tension, sometimes termed wetability or surface attraction, is an important factor in casting, hence the character of the mold is a factor.

White[4,5] made a study of the surface tension of type metals by measuring the distance different type metals would fill out a very fine opening (1 mm. dia.) in a mold under standardized casting conditions. He found that the addition of zinc to type metal cast in air materially increased the surface tension. As zinc is known to be especially harmful to type metals this seemed to lend support to the idea that the low surface tension of the type metals accounts for their good castability. However, he also found that the addition of sodium lowers the surface tension and apparently this metal does not appreciably improve the castability. In castability tests White[4] found that the composition of the metal, the casting temperature and the mold temperature are much more important in determining the castability than any differences in surface tension produced by the addition of zinc or sodium.

These castability tests were made in spiral molds of relatively large diameter so the behavior for capillary openings as in fine detail type is still uncertain. It appears somewhat doubtful, however, that surface tension plays a very important part in the good castability of the type metals. The detrimental effect of zinc may be due mainly to its injuring the mechanical properties through drossing and raising the melting point rather than through increasing the surface tension.

Cast type and stereotypes frequently contain shrinkage cavities and blowholes. Type cast in a mold is chilled very rapidly on all sides so that the portions of the type containing the cavities cannot be discarded as is done with the "pipe" in a hot topped steel ingot. All that can be done is to design the mold parts and control the casting temperature and cooling conditions so that the shrinkage cav-

Plaster Mold Broken from Aluminotype.

Pouring the Molten Aluminum.

A Perfect Impression in Plaster

ities will appear in the least harmful locations. With stereotype plates attempts have been made to apply pressure during the solidification stage and subsequently in order to close up shrinkage cavities.

In regard to blow holes very little gas seems to be dissolved in the melted type metals so that, on slow pouring into a mold, a sound ingot without blowholes is obtained. The blowholes observed in cast type or stereotypes, therefore, must be due to the rapid casting, under pressure in some cases, and to the small size of the mold openings not permitting the air in the molds to escape. Recently the application of suction or vacuum has been very successful in drawing out the air within the molds in stereotype casting and thus giving a stereotype without blowholes. Possibly similar applications of vacuum to other kinds of type casting can be made.

The foregoing indicates the wide range of metal problems encountered by those handling type metal. These should interest the metallurgist because he can contribute toward a solution, and also because some of the remedies devised for type metal problems may prove of general metallurgical application.

(To be Continued)

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A Couple of CHUCKLES

Nudists

From the notices of meetings of the Electrodepositors' Technical Society "Supper December 4, at the White Horse Hotel. The occasion will be entirely informal and dress will be optional." Dr. Blum might try this for some of the Electroplaters' meetings, but we suggest that it be started in the summer. H.W.G.

One on Us!

In the editorial in the December, 1936, issue of METALS & ALLOYS, page 330, the commentator discussing "Sponge Iron" says:

One is the introduction of certain percentages (of sponge iron) in the raw material charges of *elastic* and other furnaces producing high grade steels (italics ours).

Typographical errors can certainly give rise to ridiculous situations.

METALS AND ALLOYS IN THE

Printing Industry—III

by B. W. Gonser and S. Epstein

Battelle Memorial Institute, Columbus, Ohio

This is the third installment of a series of four on this subject. Part I was published in the January issue with Part II in February. The discussion is another in the series of articles on the general topic of the Metallurgical Needs of the Non-Metallurgical Industries.—Editor.

Electrotyping and Stereotyping

AS has been explained, most printing is not done directly from original type or cuts, but from electrotype and stereotype reproductions. Although surprisingly good reproductions can be obtained by stereotyping, electrotyping is generally acknowledged to give the highest quality printing plate.

Electrotypes are duplicate plates for letterpress printing. They may be made from type, original photoengravings, or from electrotype patterns called pattern plates, or any combination of these. A subject to be reproduced is molded into warmed wax. The surface of the wax mold is then rendered electrically conductive by graphiting and is copper plated with copper or copper and nickel, the plated shell so formed being about 0.007 in. thick. The copper shell is thus an exact reproduction of the original. It is stripped from the wax mold, trimmed, "tinned" on the back, and backed by casting electrotype metal on it. After solidification, the copper faced electrotype is brought to the desired thickness (generally 0.152 in. thick) by removing excess metal from the back, and all parts of the face are brought up to a uniform printing plane by so-called finishing operations.

As an indication of the relation between the electrotyping and metallurgical industries, it is to be noted that about 7,500 tons of electrotype metal are consumed yearly in the United States. Some of the drosses are re-smelted, adjusted to the correct composition, and returned, but this involves a metallurgical operation. About 1,500 tons of copper are also used yearly by the electrotypers. This is in the form of either rolled, cast, or electrolytic anodes, the relative consumption being on the order of 70, 30, 10, respectively. Nickel anodes of all forms are used. The 95 to 97 per cent cast anode is used by about 90 per cent of the electrotypers and high purity depolarized anodes by the

Finishing. After rough planing the cast nearly to final thickness, imperfections are corrected by hand. (Courtesy: Rapid Electrotype Co.)

Molding. The wax case is dusted with fine graphite to prevent sticking and to act as lubricant, then the printing plate to be reproduced is forced into its surface. These hydraulic molding presses exert a pressure of 200 to 400 tons but are capable of much higher pressures. (Courtesy: Rapid Electrotype Co.)

Lead Molding Press. Instead of wax, soft impression lead may be used for very high grade work on certain types of plates. Heavy pressures are needed. This press will deliver a 2000-ton squeeze...(Courtesy: Rapid Electrotype Co.)

Automatic Casting Machine. The electrotype shells are brushed with a soldering flux, strips of solder foil are melted on the backs, and a heavy backing of electrotype metal cast over them. (Courtesy: Rapid Electrotype Co.)

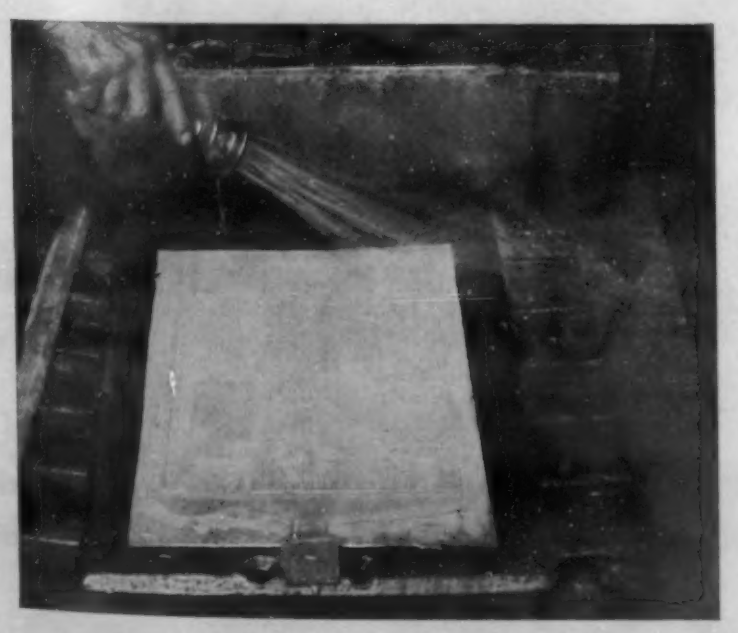
remainder. Nickel consumption by the industry probably does not exceed 50 tons yearly.

Molding

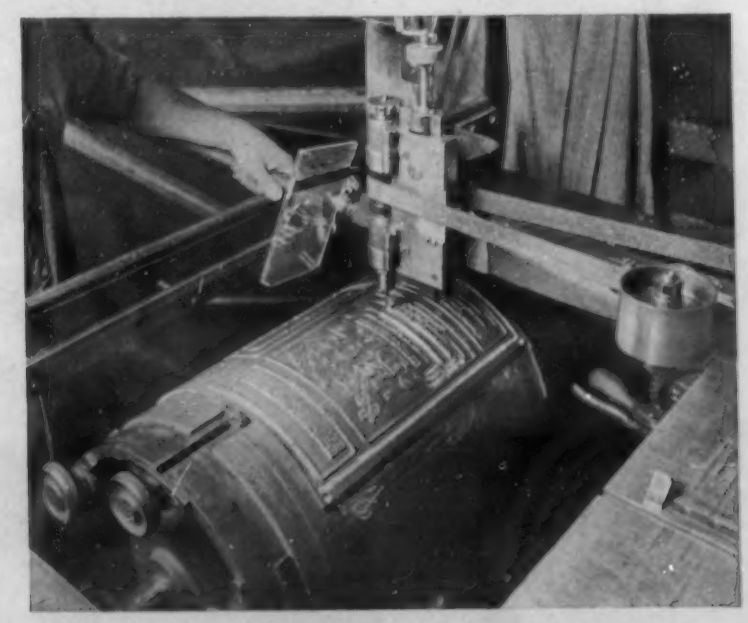
In molding into warmed wax, imperfections arise because of dimensional changes, etc., in the wax. Graphiting, the outstanding nuisance of the electro-typing industry, has to be applied to make the wax electrically conductive. For the finest electrotypes the molding is done at room temperature in sheet lead (impression lead) about 0.040 in. thick. Although this gives remarkably accurate reproductions and no graphiting is required, lead molding has the drawback that very high molding pressures have to be used (as high as 20,000 lbs. per sq. in.) which injures ordinary type and wood-mounted plates. For this reason lead molding is at present used only on properly prepared halftones and special electrotypes of type matter and not for type matter direct.

Attempts have been made to mold into thinner lead sheet in which less pressure might be required but so far this procedure has not yet been successful, and the application of lead molding for all classes of work still presents a difficult research problem. The possibility of making a softer lead seems remote since impression lead is already made very pure for maximum softness. Corroding lead is usually used for this purpose. Heating slightly during molding may result in appreciable softening. A typical analysis of the best quality of impression lead has been stated by Baker[7] to be as follows:

Coating the Case. As a final precaution to facilitate plating, fine iron filings are sifted over the mold and copper plating solution added to obtain a thin coating of freshly deposited copper. (Courtesy: Int. Assn. of Electrotypers.)



Routing. Excess metal that might interfere in printing is reduced below a printing level by routing or machining with a rapidly revolving spindle carrying a cutting tool. Done on both flat and curved plates. (Courtesy: Int. Assn. of Electrotypers.)



Electrolytic Tanks. Cases containing wax impressions or lead molds are suspended in these air agitated electrolytic tanks. (Courtesy: Rapid Electrotype Co.)

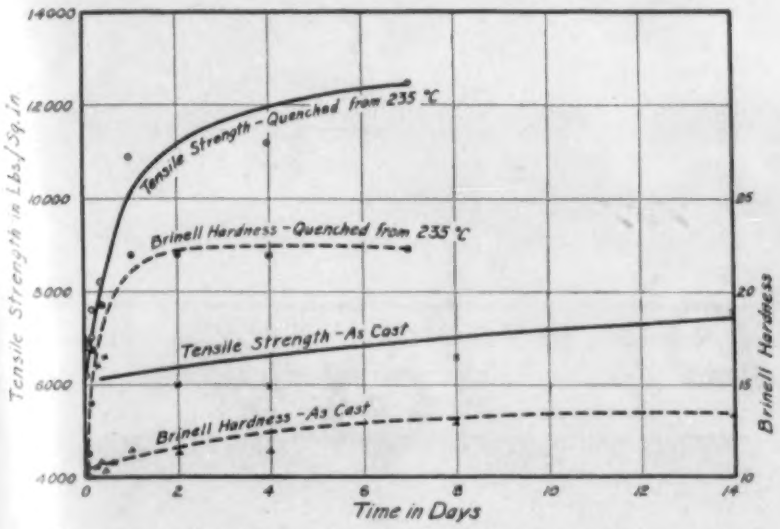
Mat Making Machines. A thick damp sheet of special paper is placed over the type matter, blankets placed over it, and the whole dried under about 100 lbs. per sq. in. pressure. (Courtesy: Rapid Electrotype Co.)

	Per cent
Aluminum	0.0001
Antimony	0.0047
Copper	0.0004
Iron	0.0007
Silver	0.0007
Tin	0.0001
Lead by difference	99.9933

It is found that the surface of pure lead corrodes to some extent in the atmosphere. To overcome this, tin coated impression lead is used to a considerable extent. A solid sheet of rolled tin is attached to one surface of the lead ingot; welding occurs during rolling and one side of the lead sheet then has a highly polished tin coating.

The solder foil used for tinning the backs of the electrotype shells is usually of the 35 tin—65 lead grade and is about 0.0015 in. thick. Up to about 1 per cent antimony does not seriously affect the fluidity of the solder. Copper, zinc, and aluminum tend to produce infusible crystals and should be avoided. The copper content should be kept below 0.07 per cent. Bismuth is not harmful, since it forms a low melting point eutectic.

Attempts have been made to eliminate the nuisance of graphiting by chemically silvering the wax molds. The



Increase in Hardness and Strength of Electrotype Metal on Aging at Room Temperature.

difficulty with this is that the silver film precipitated out of a silver solution onto the wax is very weak, tends to pull away from the wax, and to split soon after application of the current. Further attempts to solve this problem might be worth while.

Plating

The plating problems in electrotyping molds are in general similar to those in other electroplating work and good progress has been made in operating the copper and nickel solutions so as to obtain strong, ductile, uniform shells without pinholes or other defects. Longer runs are obtainable by first depositing a layer of nickel followed by copper than by plating the whole shell of copper. Sometimes several alternate laminations of nickel and copper are made to obtain desired properties. The number of impressions obtainable with different kinds of electrotypes are given below[8]:

	Average Life of Plate, Impressions
Flat copper electrotype from type-form	150,000
Flat nickel electrotype from type-form	600,000
Flat copper electrotype from half-tone	100,000
Flat nickel electrotype from half-tone	300,000
Curved copper electrotype from type-form	300,000
Curved nickel electrotype from type-form	1,000,000

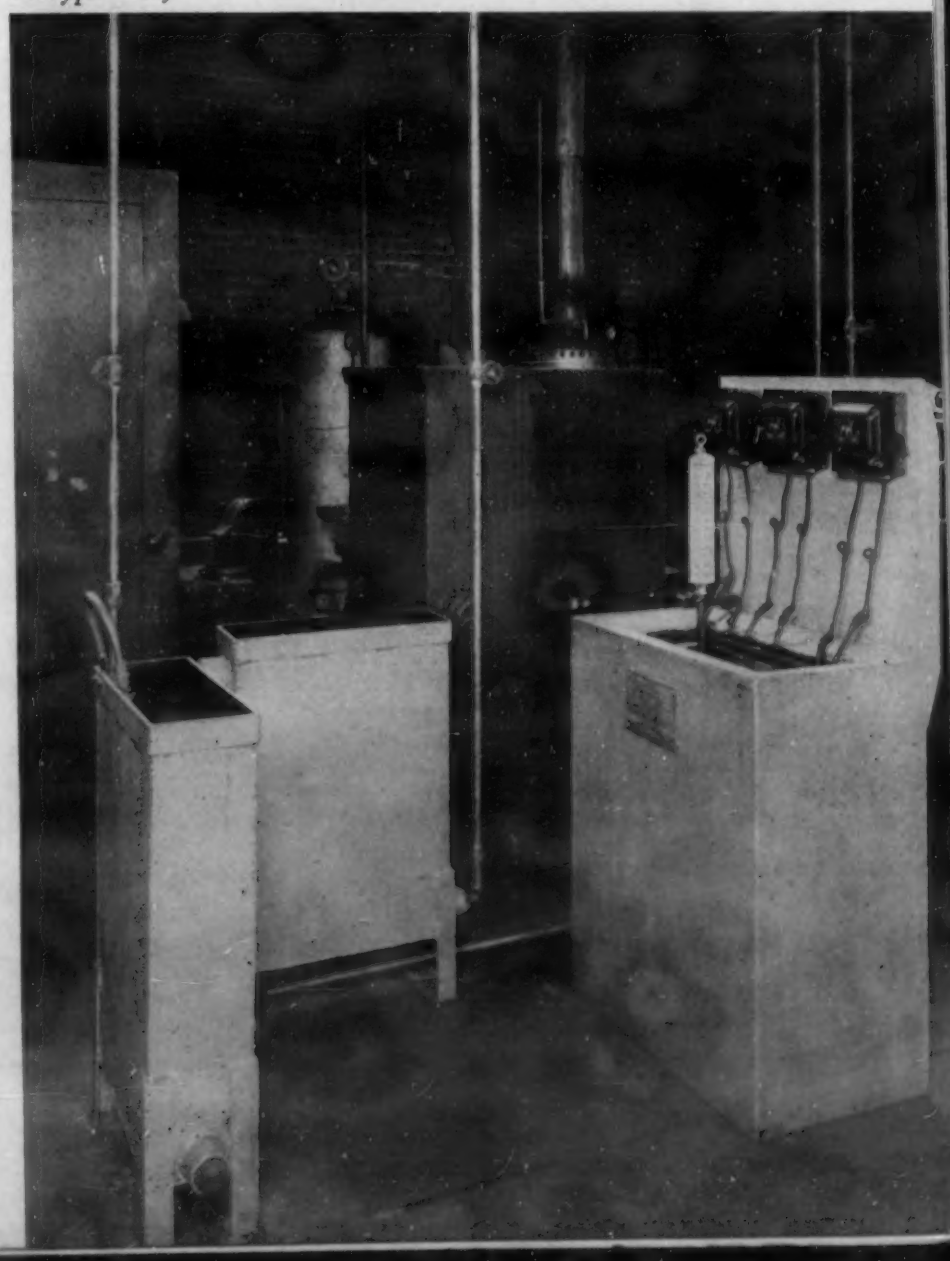
Molten Electrotype Metal Flowing into Casting Pan. The shell m be backed with 3/8 in. of electrotype metal. (Courtesy: Rapid Electr type Co.)

Curved copper electrotype from half-tone	200,000
Curved nickel electrotype from half-tone	800,000
Chromium plating over copper or nickel will double the above.	
Original zinc etching	30,000
Original copper half-tone	50,000

The values above illustrate how electrotyping increases the printing life, particularly for nickel types, the difference in life between type matter and half-tones, and the increased life of curved plates (rotary printing) over flat plates (flat bed printing).

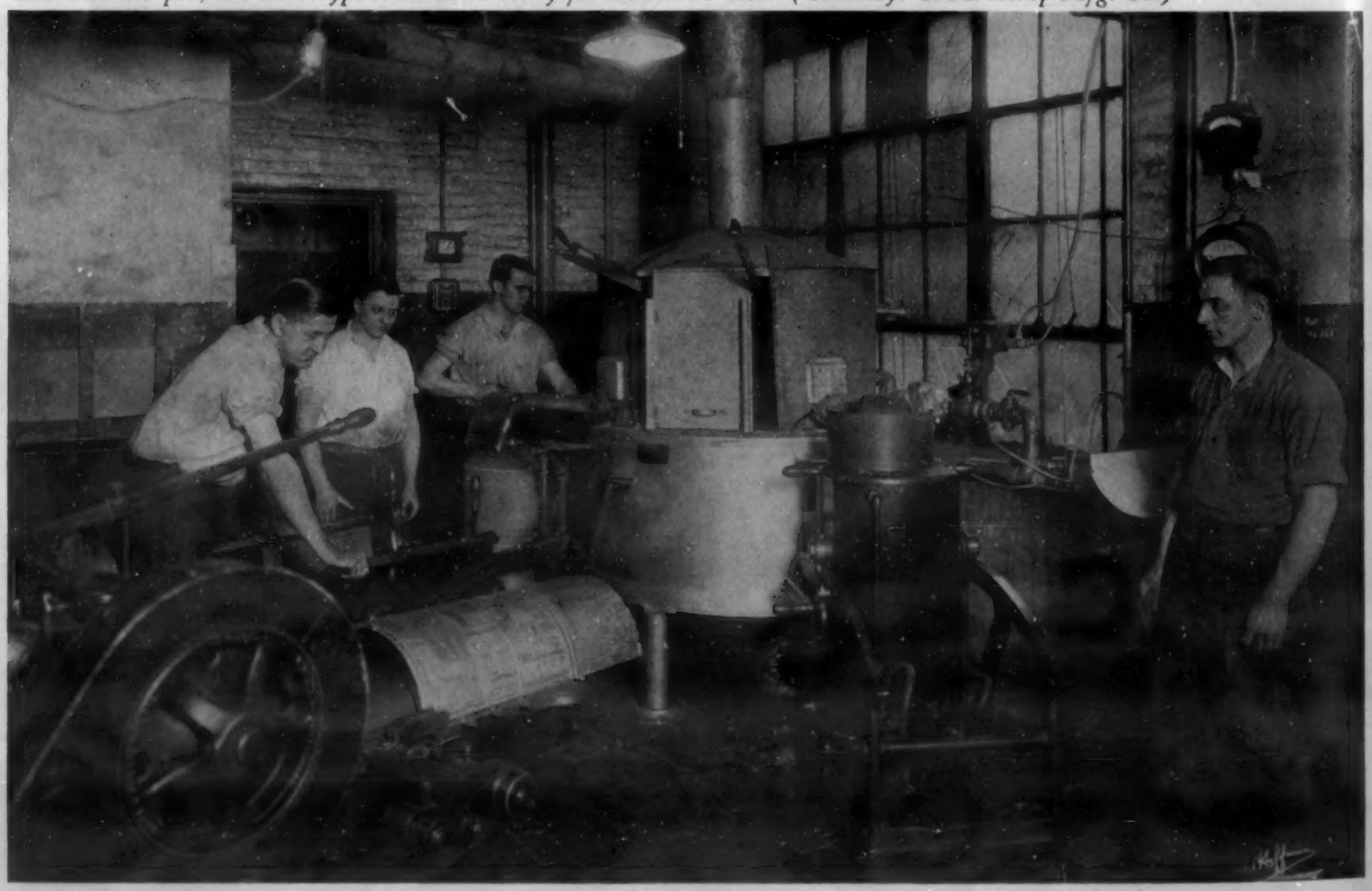
Nickel electrotypes are made by first electrodepositing nickel (0.002 in.) and then copper (0.008 in.) on the nickel coating. It is also possible to deposit nickel on the

Equipment for Heat Treating Electrotypes. An electric immersi heated oil bath at the right is used for heating the cast plates to abo 450 deg. F. They are quenched in the cold water tank (center) a oil removed in the cleaning tank at the left. (Courtesy: The Ace Ele trotype Co.)



Curving a Plate in a Lead Jacket. Electrotypes are often curved for rotary press cylinders. Usually done by protecting the face of the plate with a thick rubber blanket and passing the whole several times through a heated three roll curver. Aluminotypes and special non-stretch electrotypes are bent while encased in electrotype metal. (Courtesy: Rapid Electrotype Co.)

Casting and Cutting Stereotypes. Stereotype metal, heated in the immersion gas-fired pot in the background, is cast vertically against curved stereotype mats contained in cylindrical molds. The "tail" or excess casting is removed and tossed back into the pot; the stereotype is trimmed ready for immediate use. (Courtesy: C. M. Kemp Mfg. Co.)



A Stereotype Mat. (Courtesy: Rapid Electrotype Co.)

finished copper plate. There is a certain advantage in this, since the nickel is not abraded off in the finishing, and the heaviest nickel deposit will be where it is most needed, that is, on the printing surface of type and half-tone dots, rather than on the sides, walls, and non-printing areas. However, it is the general opinion that a nickel deposit is more satisfactory when plated directly on the mold than as a facing of the completed plate. Most electrotypers are not equipped for chromium plating and this is one reason why chromium plating is not more generally used on electrotypes. Further work on improving nickel and copper solutions and on improving the engineering efficiency of the plating operation is being considered by the International Association of Electrotypers and Stereotypers[9].

Casting and Curving

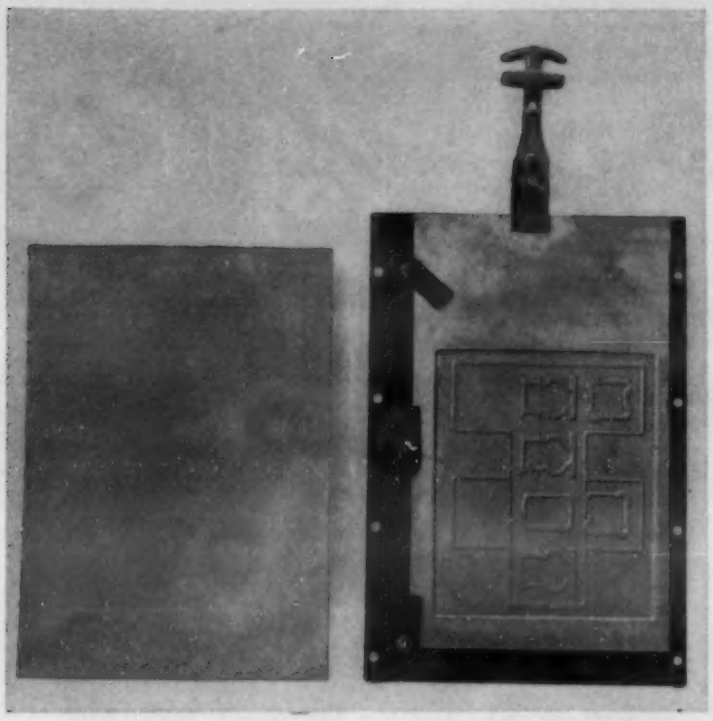
Backing the electrodeposited shell with electrotype metal, as now practised, is a simple, open-casting operation. The shell is stripped from the wax mold after loosening with hot water, a liquid flux applied, and the back covered with solder foil. It is then laid face down on a shallow casting pan which is set on top of molten electrotype metal in an open pot. This melts the solder. Molten electrotype metal is poured into the pan and over the tinned shell. Temperature of pouring is held at about 650 deg. F., the pan temperature at about 425 deg. F. The pan is set over an open air space during and subsequent to casting.

Several defects may arise during casting which make proper control of this operation important. Assuming a good solid cast with good adherence to the shell, the metal

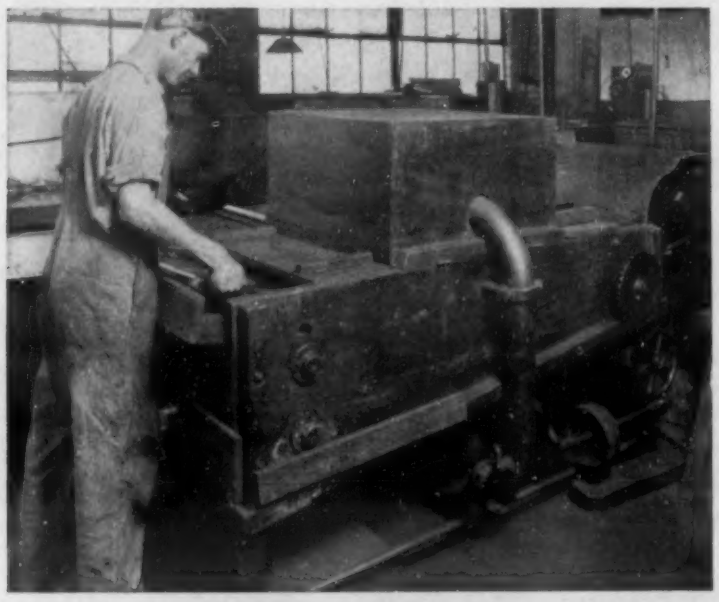
may still be coarse grained if the casting temperature is too high or if the metal is cooled too slowly. The coarse grains crinkle somewhat during subsequent curving (for rotary printing) and this will show through the shell, appearing as a "mottling" in the solids, i.e., in the solids and halftones.[10] A more serious difficulty is the distortion which takes place during solidification.

As a consequence the face of the shell is not level and expensive straightening (finishing) operations have to be applied to bring the printing face up to a true plane. Finishing is one of the most expensive operations in electrotyping. Some positive means of keeping the face of the shell in contact with the plane surface of the pan during solidification, for example, by applying suction through the bottom of the pan, should aid in materially reducing finishing costs[9].

Making the Wax Case. A thin copper sheet is coated to a depth o 1/4 in. or more with an Ozokerite base wax (m.p. about 120° F.) Before the wax cools a gas flame is played over the surface to assur a mirror like solid molding face. (Courtesy: Rapid Electrotype Co.



Lead Mold. Sheet lead before and after making the impression. Usually nickel is first deposited, then copper. (Courtesy: Int. Assn. of Electrotypers.)



Wet Graphiting Machine. Some molds are given a wet coating as well as a dry coating of graphite. (Courtesy: Int. Assn. of Electrotypers.)

Releasing a Shell from the Mold. By pouring hot water over the electro-deposited shell it is readily stripped from the wax mold. (Courtesy: Assn. of Electrotypers.)

Dimensional changes which disturb accurate register also occur during casting, but the most serious misregistering results from improper curving.

Note: For color process half-tones the extreme difference of corresponding points in the final impressions should be not more than 0.003 in. To secure accuracy of register it is necessary that the dimensions of the plates should correspond only within about 0.005 in., as the effort is always made to have plates register exactly at their centers, so that half of the error then appears at each end.

If the plate is curved cold, the outer side of the curve (i.e., the face of the electrodeposited metal) stretches, the amount of stretch being equal to the thickness of the plate divided by the outside diameter of curvature[11]. In one in-

Sawing the Cast. The cast plate usually contains several electrotypes which are separated by sawing. Graphite is scrubbed from the face of the shell before this operation. (Courtesy: Rapid Electrotype Co.)

genious method of curving which is used, the backing metal is heated to the point of incipient fusion so that it cannot exert any restraint on the shell. The effect is as though the backing were removed, and the thin copper shell then curves with practically no dimensional change. The heating also tends to overcome mottling. Where a large number of plates of the same size and curvature have to be used, it has been found feasible to cast them curved in a closed box, in a multiple casting machine. Closed casting has not proved practical, however, for ordinary commercial work because of the multiplicity of sizes and curvatures of plates, and variance in thickness.

Heat-Treated Electrotypes

As is well known the lead-antimony alloys, particularly those containing about 2.5 per cent antimony, are subject to age-hardening. By quenching from about 450 deg. F.,

(Continued on page 72)

Steel Reminiscences—III

(Continued from the January and February Issues)

by Henry D. Hibbard

Consulting Engineer, Plainfield, N. J.

MY first job as steel melter was, from 1882 to 1885, with the Norway Iron & Steel Co. in South Boston, Mass. There were three 10-ton furnaces, the usual charge being 12 tons. Practice there was like that at Nashua in that only Martin steel was made, but the wrought iron additions were hammered puddled blooms made in the plant. These blooms were low in phosphorus but contained of course considerable basic irony puddle cinder.

First Position as Open-Hearth Melter

I served first as works chemist, using my quick tests for analyzing the metal while in the furnace, but soon was made day melter in charge of the shop. The usual practice there had been to tap the furnace too soon after the charge was melted so that much of the steel was on the verge of redshortness, particularly the softer grades. The slags were dark-colored, earthy and irony and, if any was teemed on a top-cast ingot, it boiled there until frozen, as carbon continued to be oxidized. The ingots cracked more or less in the first passes through the blooming mill.

By holding the charge in the furnace a little longer before tapping, I fairly well corrected the redshort tendency, most of the ingots thereafter showing in rolling but few and small, if any, cracks. Though I did not know it then, I was in danger, in holding the charge, of trouble from too hot metal which, had it come, I would not have recognized, or have known how to correct.

We made slabs, rolled on our blooming mill, which were rolled into plates for boilers and tanks at the Bay State Iron Co.'s mill which I have mentioned. We had six important customers for spring steel who made the same kind of carriage springs. Yet each demanded a different grade of steel from the others, manifestly because their working and tempering methods were unlike. Some of this spring steel, untreated, had tensile strengths as high as 155,000 lbs. per sq. in. with 13 per cent elongation in 2 in.

Effect of High Silicon Pig

At the Norway works I had my first experience with too high silicon in the pig iron of the charge for making spring steel. To obtain the high carbon specified, a proportionately great quantity of pig was required in the charge. The bath lay dead with almost no boiling action. Though the steel had the desired carbon, the customer complained of it and I did not know how to overcome the trouble, which merely needed a sufficient quantity of ore to be added. I did add ore sparingly to later heats but not enough to wholly rectify the quality.

One experiment we tried at Norway was notable. The point had been raised by Dudley and others that silicon, as it had a stronger affinity for oxygen than manganese had, should be a more efficient deoxidizer of molten steel than the latter. The *a priori* reasoning went no further. No thought was given as to what would become of the silicic acid formed by the reaction, or what its effect on the metal would be.

The manager proposed that we should try it which I was eager to do. I added to a medium grade heat enough silicon to kill it—about 0.30 per cent as I remember. The result was total failure. The steel cast into beautiful solid ingots but it was redshort to an astonishing degree. One of the ingots was broken into myriads of pieces by one pass through the blooming mill. It had no ductility whatever when hot. Added silicon may act quite differently from residual silicon in steel as this demonstrated. An addition of manganese was also needed whose oxide would flux the silica. The fusible particles formed would then coalesce and, more or less completely, depending largely on the time allowed, be floated up to join the slag.

When I began work at Norway, the siemas there were built wholly of clay bricks which lasted for about 50 heats. Later we had silica bricks for the roof and walls of the melting chamber which were of course far more durable.

Oil and Gas as Fuels

Before I had charge there, a trial was made of melting steel with oil as fuel. The oil was gasified by feeding it with some air into a red hot steel vessel. Without air the vessel would have become clogged by carbon deposit. The gas formed then flowed to the melting furnace. It was somewhat like producer gas. The method proved to be too costly and was discontinued before I took charge. There, as at Nashua, the melting was done solely by producer gas.

Turns to Copper Industry

In 1885 and 1886 I digressed from steel to go to Butte, Mont., for the Parrot Silver & Copper Co., which had installed the Manhes process for the pneumatic conversion of copper matte into metallic black copper. It was the first commercial plant of its kind, though Manhes had worked the process experimentally in France. He did not understand his own invention. He was troubled by cold heats, to avoid which he claimed that higher matte was needed, stating 72 per cent Cu in the matte as suitable. He could not get such matte and his heats worked cold, so to get more heat in his charge he added coke in the converter

which may have helped but did not cure the trouble. At the Parrot plant the same trouble from cold heats was experienced and the same method tried, but skulls in the converter and irregular shape and weight of the ingots was common. Too much scrap copper was made.

Before going to Butte, I felt that probably, from the point of heat supply, iron and sulphur in the Manhes converter would act somewhat as silicon and carbon do in the Bessemer steel process. That proved to be the case. Silicon in the Bessemer process and iron in the Manhes burn to non-volatile products which remain in the vessel, raising the temperature there. But carbon in the one process and sulphur in the other burn to gases which, leaving the vessel, carry off heat.

Iron in Copper Matte

At Butte I at once started to determine the percentage of iron needed in the matte to give hot enough heats and found it to be 14 per cent, which in our matte was that containing 62 per cent Cu. So I directed that thereafter no matte richer than 62 per cent should be made. That was easy as, however rich the roasted ore and concentrates were in copper, we had plenty of raw concentrates, all sulphides of copper and iron, to add to the charge, to lower the grade of matte as desired, whether smelted in cupola or reverberatory furnace. With iron not less than 14 per cent, the heats poured cleanly from the vessel to the molds making clean ingots with a minimum of scrap. No ladle was used. Now, of course, much lower mattes are blown successfully.

One day, getting a whiff of gas from the copper converters, I noticed that it was more pungent than sulphurous acid, SO_2, which results from burning sulphur in the open. Later I mentioned this to the late Richard Pearce of Denver and he offered the explanation that some of the sulphur was probably burned to sulphuric anhydride, SO_3, which I have always accepted as correct.

While I was in Butte, Eli Perkins, who was something of a globe-trotter, came there, and, after examination, he pronounced it the wickedest city on earth. Murders were frequent. When I went from the city to the smelter, about one mile, after dark, I walked in the middle of the road with my revolver in my hand, but the only time I used it was when attacked by a dog, whom a bullet sent off yelping.

One day a dense fog or cloud settled on Butte and vicinity, and, by screening everything, checked nearly all outdoor activities. A man on horseback could not see the ground, but had to dismount and lead his horse being barely able to see the trail by stooping down. Walking, I nearly bumped into a house which I did not see until almost within touch.

(To be continued)

(Continued from page 70)

hardness of electrotype metal can be doubled over that of the cast condition. Practical use is being made of this phenomenon in obtaining harder electrotypes which are less subject to washing in the press, which will stand larger runs, and which can be used for severe stamping and embossing operations[12]. It is also considered that a stronger, heat-treated plate with a higher endurance limit may overcome fatigue cracking which sometimes occurs on the press.

Of course, higher antimony and hence harder backing metal than electrotype metal could be used instead of heat treating. This is subject to many disadvantages, however, because a higher antimony metal is more expensive, does not adhere to the shell as well, is subject to segregation during the rather slow cooling in the pan, and is too hard and brittle for ease in finishing. The great advantage of hardening by heat treating is that the plate can be finished while it is still in the soft and ductile condition. Since one of the disadvantages of stereotyping is that stereotype metal is in general too brittle for finishing, possibly heat-treated electrotype metal could be used for this purpose, wherever there is time for aging to occur.

Stereotyping

Marked improvements is stereotyping have occurred recently because of the insistent demand for cheaper letterpress printing. Average quality stereotyping can be done for about one-half the cost of electrotyping. A fair quality half-tone work is possible with nickel-faced or chromium-faced stereotype plates of the better grade. The cost of preparing material for the highest grade stereotypes is very great and thus the resultant stereotypes cost as much as or more than electrotypes.

Two important developments in stereotyping might be mentioned here, that of vacuum casting, and that of solidifying under pressure to eliminate shrinkage and to get more perfect reproduction.

In vacuum casting, the stereotype mat paper is placed on one side of the perforated wall of the vacuum casting box, a paper guard against the other perforated wall, and the stereotype metal is cast in between, under vacuum. A very solid casting with virtually no blowholes is obtained.

In the process to eliminate shrinkage, the paper mat is stretched over the type-form, locked, and the impression made by molding in a press. The back of the stereotype mat is shaved flat while still in contact with the form. The mat is then cast in a box, the shaved side being flush against the flat machined surface of the box. Pressure is applied after the metal is poured into the box by raising up a wedge-shaped copper strip, thicker at the bottom than at the top, in order to squeeze the stereotype metal solid during the mushy stage. At the same time a more perfect impression is obtained. Very close temperature control of the mat, metal, and box is maintained, and superior control of register on color work is claimed.

For high-speed newspaper printing the cylinders rotate so fast that the centrifugal force tends to spread out the stereotype plates giving smudge printing. A stronger and lighter stereotype metal would be helpful here, for example, the practical development of the zinc-aluminum type metal alloys. So far this matter has been handled mechanically by incorporating ribs in the stereotype plates to reduce the bulk and by using various holding devices for attaching the plates to the press cylinders.

(To be concluded)

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AN X-RAY STUDY OF PREFERRED

Orientation in Rolled Copper

by H. V. Anderson and G. L. Kehl

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The limitations of the preferred orientation in rolled copper has been studied by two X-ray diffraction methods. One method, suggested by Dr. W. P. Davey, consisted of obtaining a diffraction pattern of the specimen by "surface reflection"; the other method by transmission of the X-rays through thin sections of the specimen.

The samples employed were electrolytic copper that had been subjected to light and heavy roll reductions by both straight rolling and reversed rolling.

The surface orientation of the specimens was examined by the reflection type method and the results showed that straight rolling produced the same amount of preferred orientation as reversed rolling, for both heavy and light roll passes.

The transmission patterns obtained from thin sections of the specimens indicated that below the original surface layer, reversed rolling produced a more random orientation than straight rolling without apparent regard to the severity of roll reduction.

WHEN A METAL IS SUBJECTED to a rolling operation, the individual grains or crystals tend to be broken up into smaller crystals. Accompanying this breaking up is a motion of rotation such that each crystal tends to fall into a system of preferred orientation which has a definite angular relation to the surface of the metal. The rolled crystals may orient themselves with respect to the axis of the rolls or to the rolling direction, or both.

If X-rays are impinged onto a tilted specimen[1] and a photographic plate is placed behind the specimen, perpendicular to the incident beam, a diffraction pattern will result, consisting of rings or intensified arcs. If the crystals of the metal under examination are relatively small and are in a random orientation, the diffraction pattern will consist of smooth, continuous rings. Larger crystals, still in a random orientation, will produce rings composed entirely of spots, evenly distributed over the rings. A preferred orientation will not give rings that are smooth, but a concentration of spots, resulting in intensified arcs. From the very nature of X-ray diffraction, the shorter the arcs, the higher the degree of preferred orientation. However, the smoothness of the intensified arcs will depend upon the relative size of the crystals.

The study of preferred orientation[2] is of great importance from two points of view. One is the possibility of better understanding the lattice forces within a metal; and the other, the changing physical properties of a metal when cold worked. The deformation of a single crystal takes place by a shearing motion along one or more of the crystallographic planes. This shearing will usually take place along the family of planes that have the largest interplanar spacings, since it is between these particular planes the attraction of the atoms for the atoms on adjacent planes will be at a minimum.

Hollabaugh and Davey[3] have shown that the preferred orientation of rolled nickel and copper are identical in every respect, and that as the number of passes through the rolls increases, more and more of the crystal fragments are rolled into a preferred orientation. However, from the pass after which the noticeable orientation first begins to take place, the angular limits of the preferred orientation range remain constant for all succeeding roll passes.

Scope of Investigation

The purpose of this investigation was to determine whether or not straight rolling, as compared to reversed rolling for both heavy and light roll passes to the same total reduction, had any influence on the amount of preferred orientation produced on and below the original surface.

Samples Studied

Four samples of rolled copper were employed in the investigation. All samples were rolled by Revere Copper & Brass, Inc., Rome, N. Y. The chemical composition of the electrolytic copper used was:

Copper, 99.93 to 99.94
Oxygen, 0.04
Arsenic, sulphur, etc., Remainder

Sample No. 1 was rolled from a sheet at 0.168 gage

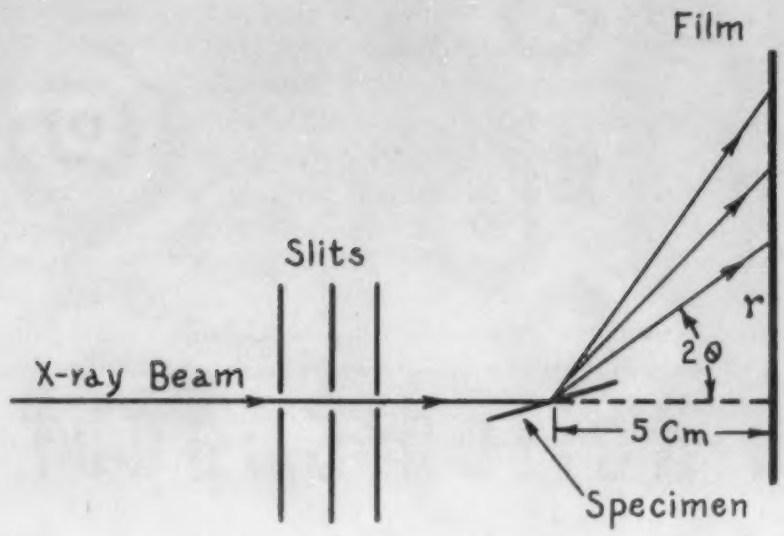


Fig. 1

down to 0.050 gage by a series of seven passes, each pass giving a 10 per cent reduction. In addition, the sample was reversed end for end for each pass.

Sample No. 2 was rolled from the same sheet as Sample No. 1 by the same 10 per cent reduction in each pass, except the rolling was done in one direction. That is, the same end of the sample was entered into the rolls for each pass.

Sample No. 3 was rolled in the same manner as Sample No. 1 (reversed rolling) except the final gage was reached in four roll passes.

Sample No. 4 was rolled in the same manner as Sample No. 3, except the direction of rolling was always the same as was the case with Sample No. 2.

Sample No. 1 and 2

Pass No.	Resulting Thickness—inches
0	0.168
1	0.151
2	0.134
3	0.117
4	0.100
5	0.084
6	0.067
7	0.050

Sample No. 3 and 4

Pass No.	Resulting Thickness—inches
0	0.168
1	0.120
2	0.081
3	0.065
4	0.050

Apparatus and Technique Employed

All diffraction patterns were made on a General Electric diffraction apparatus, equipped with a Coolidge molybdenum target X-ray tube. The X-ray beam was defined by a series of pin-hole slits, and to insure nearly monochromatic radiation, ZrO_2 filters were employed.

As suggested by Davey[1], the diffraction patterns were obtained by diffracting the incident beam from the surface layers of the specimens. The specimens were tilted approximately 15 deg. to the horizontal, such that the incident beam struck the middle of the specimen and a diffraction pattern registered on a photographic film placed 5 cm. from this point and perpendicular to the incident beam.

Inasmuch as no calculation would give the exact angle at which to set the specimen, it was a matter of trial until the correct angle was found. By examining a few trial exposures, it was found an incorrect angle would give elongated spots or a wide diffraction ring, and this condition would exist until the specimen was further tilted to a new angle.

It was reasonable to assume[4] that the X-rays responsible for the diffraction rings on the film came from a layer not more than 0.0004 in. deep, measured perpendicular to the surface of the specimens.

Two sets of surface "reflection type" diffraction patterns were made of each sample. One pattern of each sample was taken with the sample so placed that the direction of rolling and the incident beam were in a plane perpendicular to the surface of the specimen. In other words, the incident beam was impinged along the direction of rolling. Another set of patterns was taken with the beam impinged across the direction of rolling. An exposure of 72 hrs. was found necessary to give a satisfactory pattern without the use of intensifying screens. After a diffraction pattern had been made, the specimen was removed from its holder, and the incident beam allowed to strike the film for 10 sec., thus registering a zero point.

Transmission patterns were made of each sample, the X-ray beam passing through the specimen perpendicular to the surface. A photographic film was mounted 6 cm. from the specimen, perpendicular to the X-ray beam. The transmission specimens were prepared from the original samples by a careful etching with cold nitric acid to a thickness of 0.0098-0.0100 in. An exposure of 48 hrs. was found to give satisfactory patterns.

Attainment and Study of Results

Positive prints were made of all the diffraction patterns. The "reflection type" prints were mounted on stiff pasteboard to facilitate handling and making the necessary notations on the print. On all the patterns taken with the beam impinging along the direction of rolling, it was found that there was no indication of preferred orientation, and consequently the patterns were of no use in our investigation except to check the planes responsible for the diffraction rings and compare these with those found on the across direction of rolling patterns.

The patterns obtained with the X-ray beam impinging across the direction of rolling showed a decided preferred orientation. By very carefully measuring the radii of the arcs, the zero point caused by the undeviated beam serving as the center, the planes responsible for the arcs were calculated.

Referring to Fig. 1, it can be seen that $r = 5 \tan 2\theta$, where r = radius of each individual arc, and 2θ the angle between the incident beam and the diffracted beam. By the use of the above equation and Bragg's law, the planes responsible for the diffracted arcs could be calculated.

Fig. 2 is typical of all the diffraction patterns obtained with the X-ray beam impinging across the direction of rolling.

Calculated Planes of Diffraction Rings

Ring No.	Radius-Cm.	d_{hkl}	Indices
1	3.25	1.266	$200_{(3)}$
2	4.05	1.077	$110_{(3)}$
3	4.27	1.038	311
4	5.36	0.901	$111_{(3)}$
5	6.20	0.832	331
6	6.55	0.808	$210_{(3)}$

As shown in Fig. 2, lines were drawn from the zero point through the extremities of the intensified arcs and the angle which these lines made with each other for each particular arc was recorded. This procedure was followed for all prints.

Discussion of Results

Inasmuch as the angles between the respective arcs were the same for all the "reflection type" patterns and the intensities of the corresponding arcs were practically identical, it was evident that neither the method of rolling nor the severity of rolling to the same total reduction had any influence on the amount of preferred orientation produced. Since the "reflection type" patterns were obtained from a surface layer not more than 0.0004 in. deep, this conclusion held only for the original surface.

It was reasonable to believe that a reversed rolling operation should produce a more random orientation than straight rolling. As the specimens are reversed end for end after each pass, more and more of the crystal fragments are broken up, but the fragments tend to arrange themselves in accordance with the pass direction. That is, the fragments are rocked back and forth until the final roll pass, ultimately producing a more random orientation than straight rolling where the crystal fragments are always rolled in one direction.

However, as mentioned heretofore, the "reflection type" patterns indicated no differences in the preferred orientation on the surface layers of the various specimens. The transmission patterns obtained from the specimens whose original surface had been removed by a cold nitric acid etch,

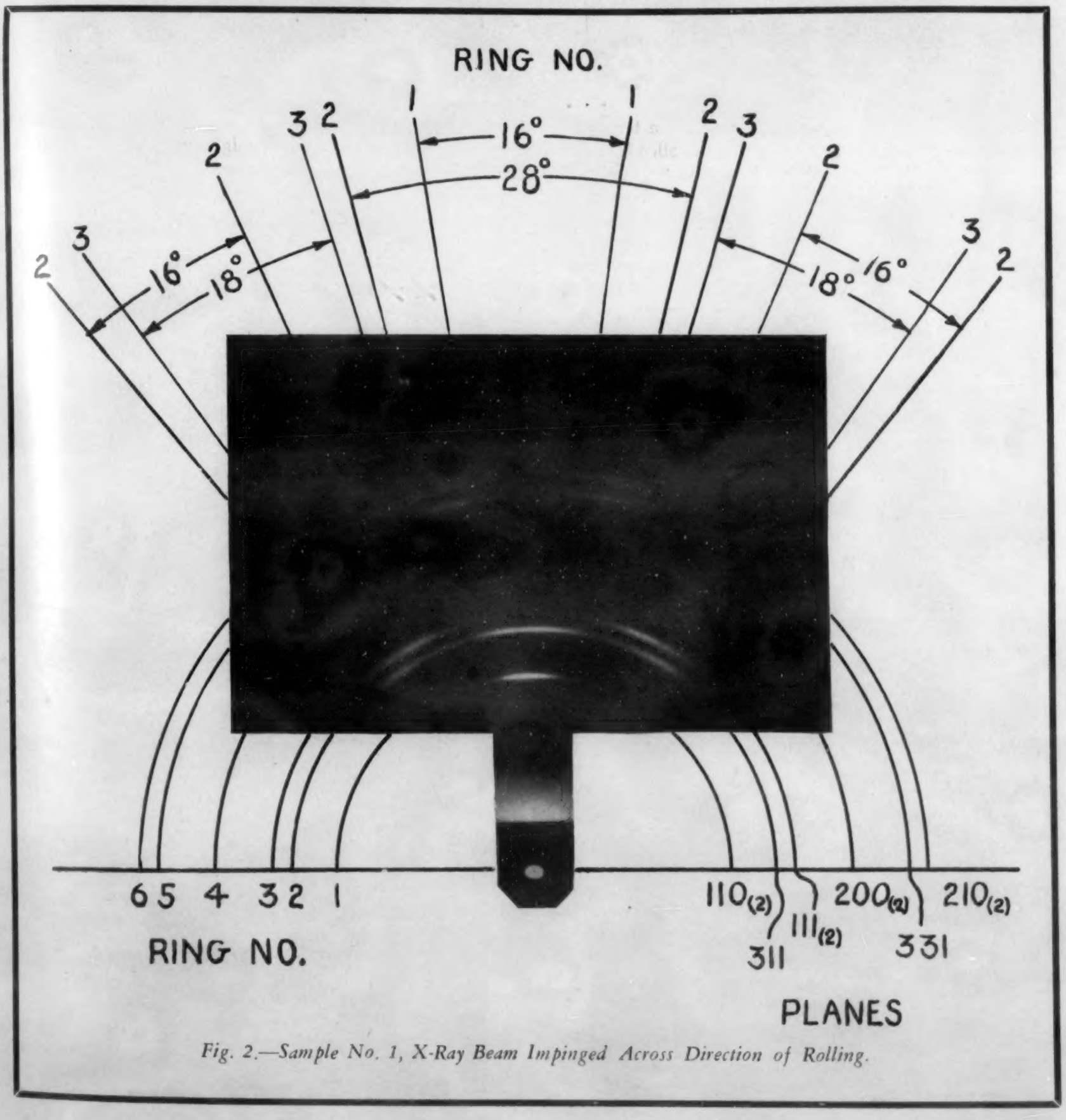


Fig. 2.—Sample No. 1, X-Ray Beam Impinged Across Direction of Rolling.

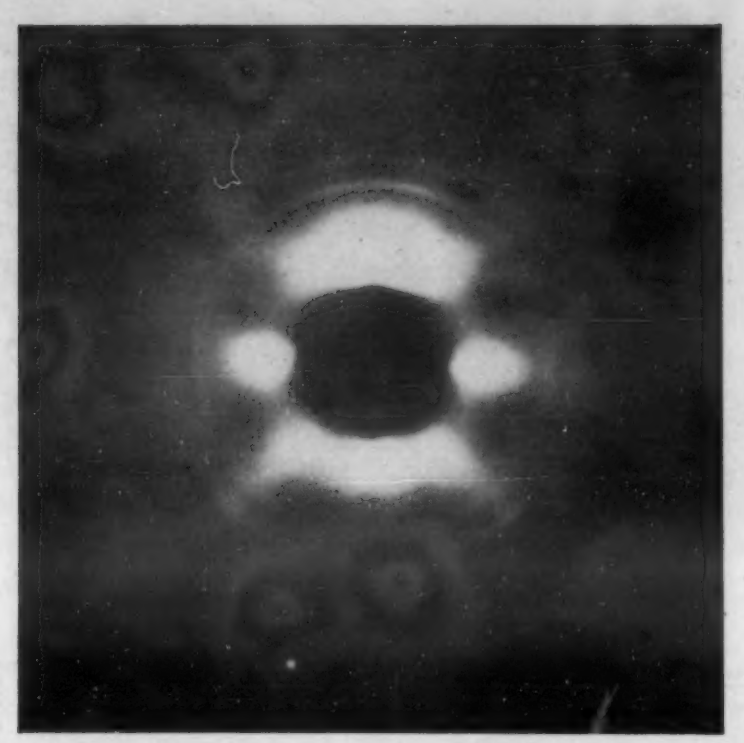


Fig. 3.—Sample No. 1, Reverse Rolled—7 Passes.

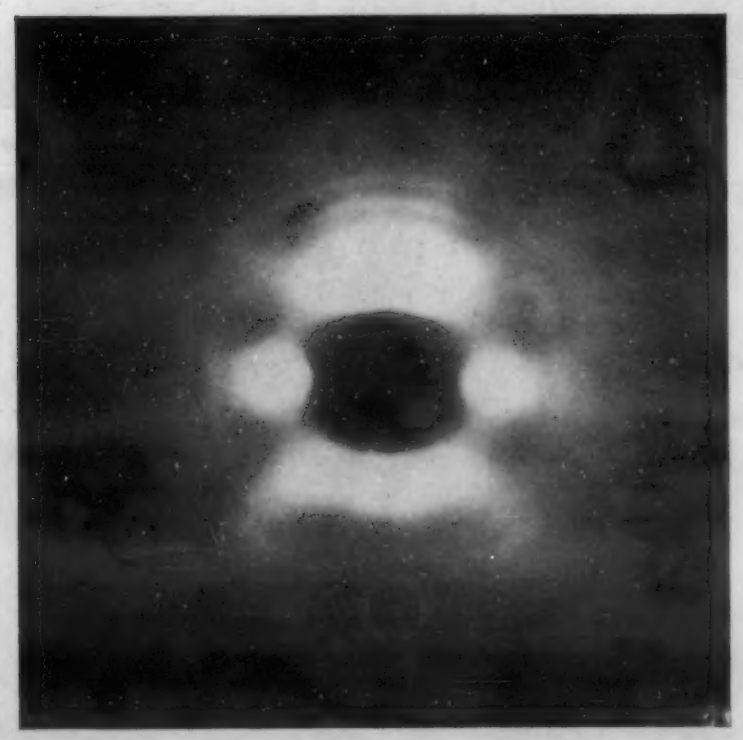
showed a more random orientation existing in those specimens rolled by reversed rolling than those rolled by straight rolling. Our conclusions were based on Figs. 3, 4, 5, and 6, which show evidence of two concentric rings in Figs. 3 and 5, which are not to be found in Figs. 4 and 6. The presence of these two rings is indicative of a more random orientation. In examination of the films, there were no apparent differences to indicate that the severity of roll reduction had any influence on the resulting orientation.

Summary

The results indicate that the amount of preferred orientation produced on the surface of rolled copper is not influenced by the method of rolling, provided the total reduction is the same.

The transmission patterns show that below the original surface (at least below 0.0004 in.) a more random orientation is produced by reversed rolling than by straight rolling.

Fig. 5.—Sample No. 3, Reverse Rolled—4 Passes.



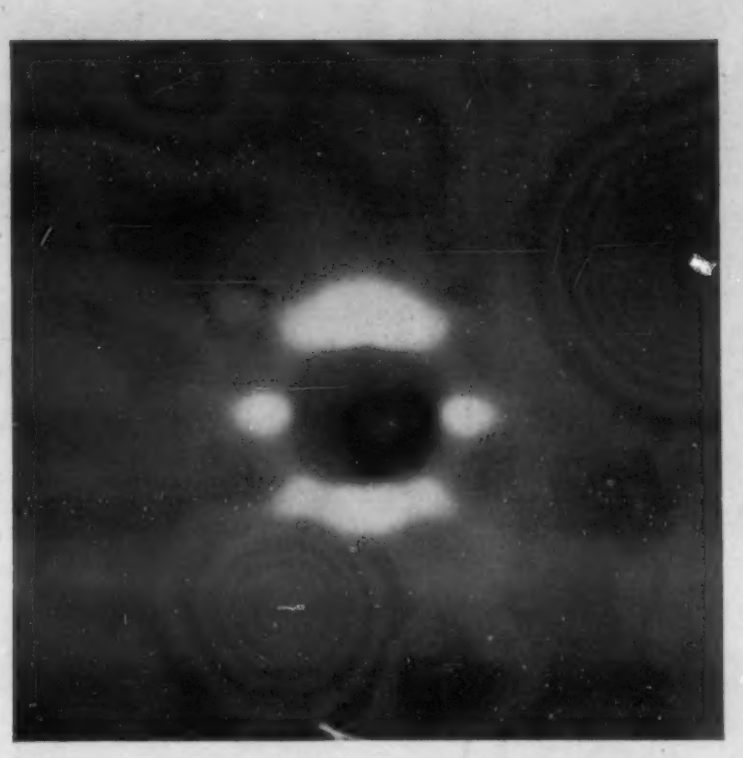


Fig. 4.—Sample No. 2, Straight Rolled—7 Passes.

The severity of rolling to the same total reduction by both reversed rolling and straight rolling has no influence on the amount of surface or interior preferred orientation produced.

Acknowledgment

The authors wish to thank L. G. Glesmann of Revere Copper & Brass, Inc., for kindly furnishing the necessary specimens and cooperating throughout this investigation. Also, the authors are greatly indebted to Dr. Wheeler P. Davey, Pennsylvania State College, for suggestions and constructive criticism.

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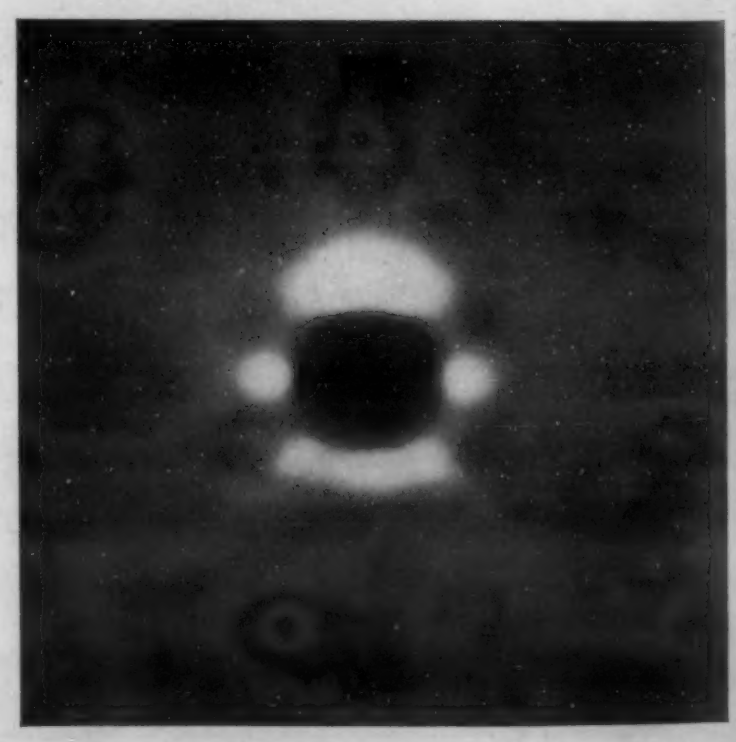
[3] Ibid. *Metals and Alloys*, Vol 2, Nov. 1931, page 307.

[4] Ibid. *Metals and Alloys*, Vol. 2, Oct. 1931, page 250.

Fig. 6.—Sample No. 4, Straight Rolled—4 Passes.



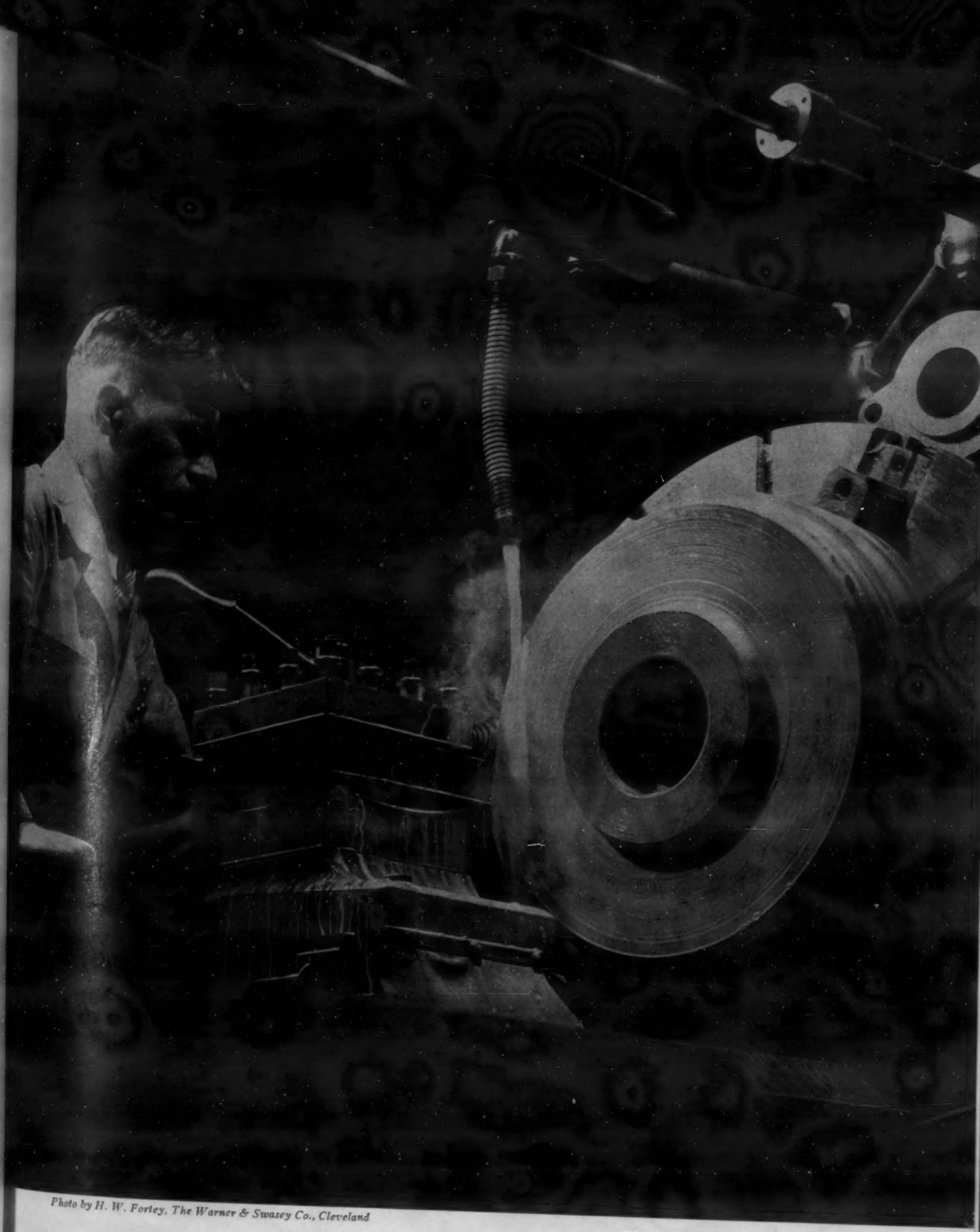
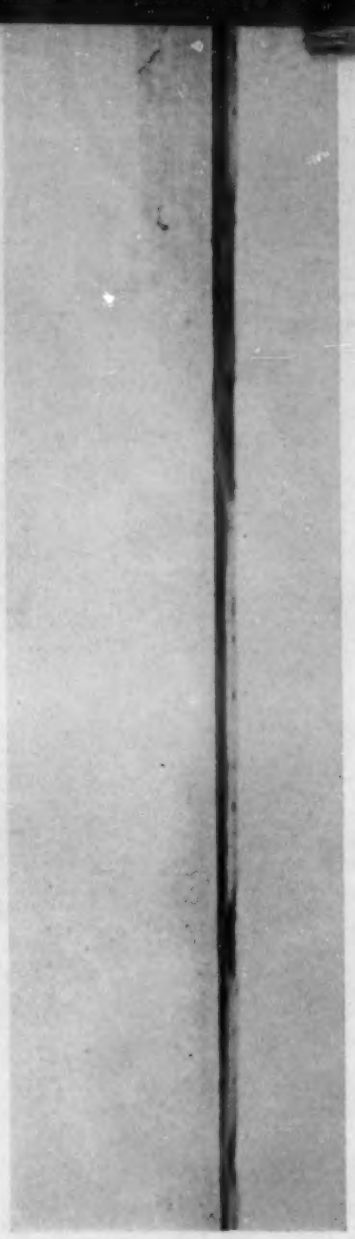


Photo by H. W. Fortey, The Warner & Swasey Co., Cleveland

Heavy Duty Turret Lathe at Work Removing 60 Cu. in. a Minute of an S.A.E. 1035 Steel Forging. Pressure on the cutter is nearly 15,000 lbs.



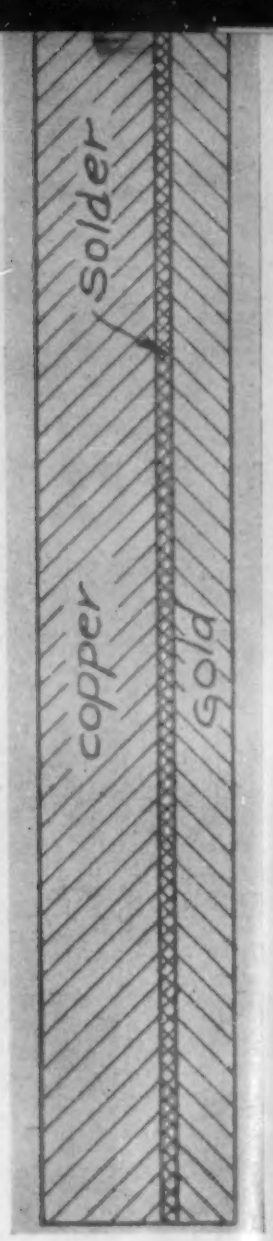


Fig. 1.—Radiograph of a Soldered Composite Copper-Gold Plate. Fig. 2.—Macrograph of a Cross Section between the Two Points A and A in Fig. 1. Etched with ammonium persulphate. Magnification 5X. Fig. 3.—Drawing of Cross Section of Composite Plate.

RADIOGRAPHY OF

Composite Gold Plate

by W. J. Wrighton and Tracy C. Jarrett

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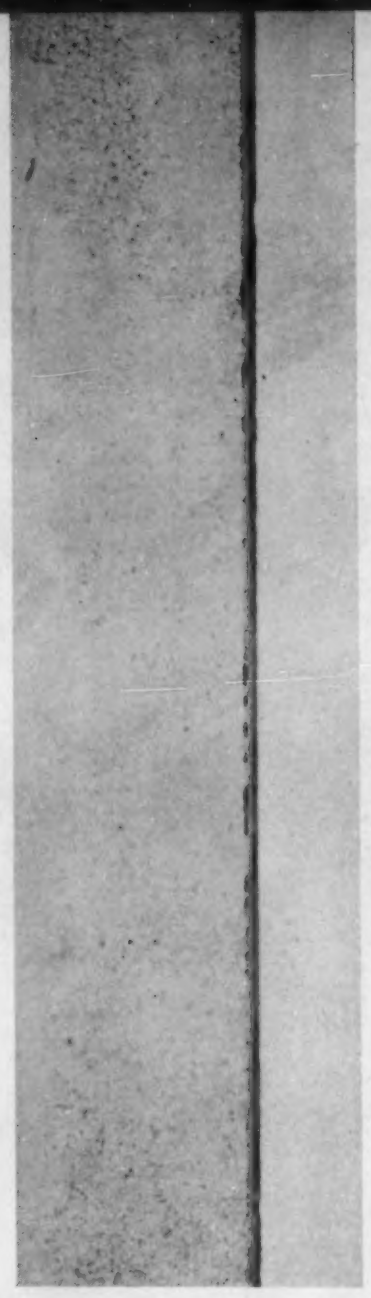
RADIOGRAPHY TODAY has proven to be of great value in industry. Although it has been applied generally to the ferrous and non-ferrous fields, it is the object of this article to show how it can be of value in the field of precious metals.

In making a study of metal castings radiography is of great value in developing the technique. A similar study can also be applied to the soldering of two dissimilar metals.

The operator in charge has certain conditions that are easily controlled, while others are very difficult. It is possible by the use of radiography to study these uncertain conditions which will lead to proper technique. In the soldering of a composite gold plate the operator has but the measured temperature of the furnace and his eye to judge when the job is finished. In a great many cases the plates look as if they were well soldered, but upon further investigation, as revealed later, this is not the case.

Fig. 3 is a cross sectional view of a composite gold plate that shows how the assembly is made, the solder being placed between the gold and copper base plate. The gold plate is about 1/8 in., the copper plate about 1/4 in. and the sheet of solder a few thousandths. The assembled plates are then placed in steel clamps and heated at a temperature sufficient to allow the solder to become molten, thus joining the two plates. After soldering and while still hot, the assembly is placed in a press and pressure applied, forcing the two plates into a more intimate contact.

A radiograph of a composite plate is shown in Fig. 1, with the cross section taken between the two points A and A. Throughout this entire radiograph, more or less dark



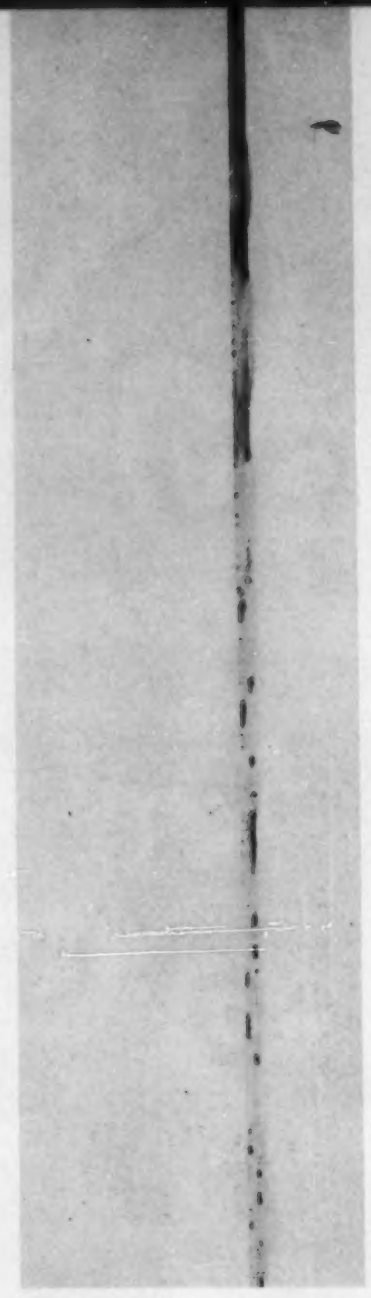


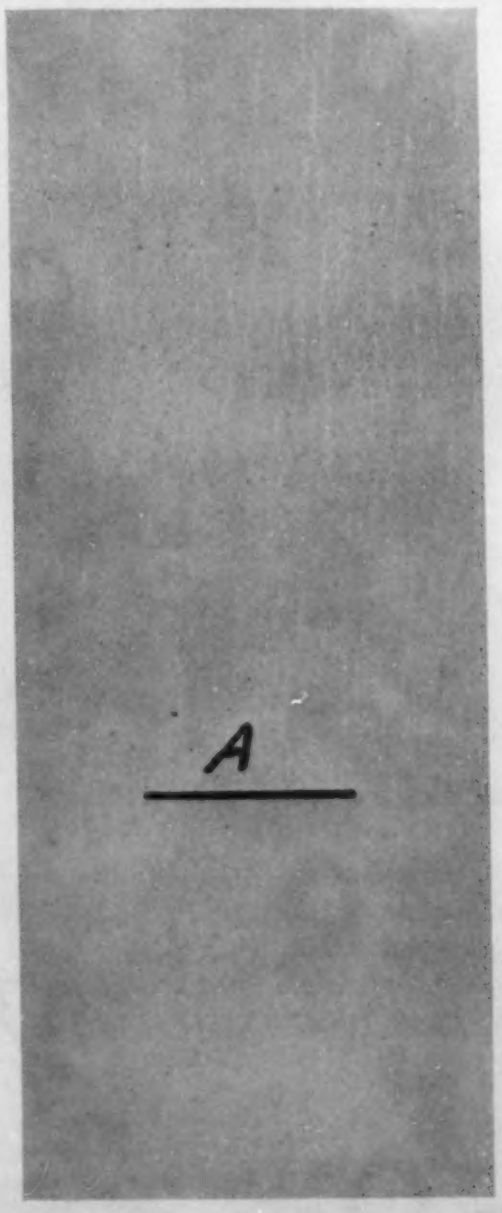
Fig. 4.—Radiograph of Soldered Composite Copper-Gold Plate. Fig. 5.—Macrograph of Cross Section Just Above and Parallel to Line A. Etched with ammonium persulphate. Magnification 5 X. Fig. 6.—Macrograph of Cross Section between the Two Points A and A. Etched with ammonium persulphate.

streaks and spots are noticed with a very pronounced portion between the points A and A. The macrograph, Fig. 2, actually shows that the sheet of solder between the plate was not molten at the soldering temperature. In portions of this cross section where the solder did flow, a porous condition exists. In all cases it is practically impossible to detect a porous condition from the external surface.

Fig. 4 is a radiograph of another soldered plate, showing a similar porous condition. In this case a very marked diagonal streak is noticed above the line A and a rather large blotch between the points B and B. The macrograph (Fig. 5), a diagonal cross section immediately above the line A, shows a porous condition. Fig. 6, a cross section taken between the points B and B, reveals a similar porous condition.

The radiograph, Fig. 7, shows a sound composite plate soldered in a similar manner, but with a slight variation in the technique. The macrograph of the cross section taken just below the line A is shown in Fig. 8. The solder line in this case is very sound and appears very even throughout the entire plate. This plate would fabricate perfectly.

From the brief data presented here, there is emphasized the great possibilities radiography can play in governing and obtaining the proper technique. It is possible, by the use of radiography, to prevent the actual destruction of the plates themselves.



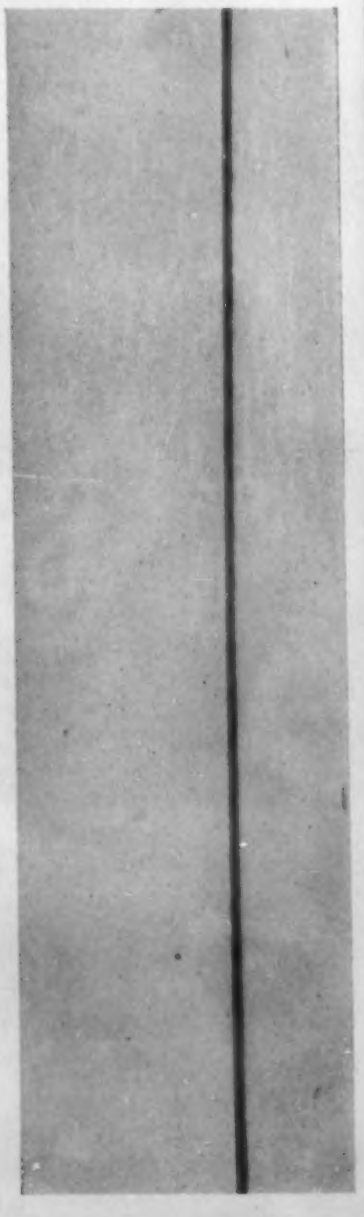


Fig. 7.—Radiograph of a Soldered Composite Copper-Gold Plate. Fig. 8.—Macrograph of a Cross Section Taken Just Below and Parallel to Line A. Etched with ammonium persulphate. Magnification 5 X.

Courtesy: Climax Molybdenum Co.

Producing Ferromolybdenum by the Silico-Thermic Process. A refractory lined iron vessel is placed on a sand bed over a hollowed-out depression. The roasted molybdenite concentrate, together with other necessary materials, is fed into the vessel, while the reaction proceeds, which takes place at around 4000 deg. F. The vessel is then lifted and the slag runs out, leaving the large button of Fe-Mo.

A NOTE ON THE DEPENDENCE OF

Microhardness on the Speed of Cutting

OF DUCTILE METAL

by Harold C. Hodge

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IT IS UNUSUAL TO APPLY the "microcharacter," or other scratch hardness determinations, in metallurgical problems involving the softer metals and alloys. In dental metallurgy, however, the specimens may sometimes be very small so that scratch hardness methods may be useful at times. In such cases the problem of reliability and reproducibility of the test arises.

In a series of scratch hardness measurements on a pure silver bar, two cuts were made by hand and one using a machine drive set-up, the former being relatively rapid and the latter relatively slow. Inasmuch as the average microhardnesses found from the hand cuts were 70 and 69, respectively, while that from the machine cut was 62, and inasmuch as silver is known to be extremely ductile which perhaps would account for the production of a wider cut by slower cutting, due to the flow of the metal, it was of interest to repeat the procedure, cutting at known speed variations to find (a) if the difference in average width between cuts made rapidly and slowly is reproducible and (b) if the average width of cut is a function of the speed.

Because the data at any given rate (see Table) are so limited, this report is not expected to provide a final word on the microhardness—speed of cutting relation for pure silver. However, it is important to call attention to a factor which may influence the reproducibility of microhardness values of certain materials with the hope that the problem may be fully investigated and standard procedures recommended.

Method

The machine driven cuts were made using the set-up illustrated previously[1] which consists of a "program switch" electric motor, mounted with a chain and sprocket drive to the micrometer screw of the microcharacter. The hand cuts were made by turning the crank on the microcharacter meanwhile watching closely an electric clock whose revolving second hand permitted a close gage of the speed of cutting. Parallel microcuts were made in the same direciton and located closely enough together to do away with the influences of gross differences in the bar. The cuts were 30 to 40 mm. long and approximately 1 mm. apart. Width readings were made at intervals of approximately 1 mm. From a graphical study of the widths along the various cuts plotted against the distance along the cut, two inferences were drawn: (a) that there was little or no dependence of width on the position along the cut, and (b) that duplicate readings on the same cut (although made on different days) were recognizable as such (compare D and D*, F and F*, in the Table).

Table of Data at Any Given Rate

Microcut number	Number of readings	Average width (μ)	Average microhardness	Rate of cutting (mm. per min.)
E	28	13.0	59	0.3
B	30	12.7	62	0.4
D	31	13.0	59	0.4
D*	33	12.9	60	0.4
O	53	12.3	66	0.4
N	24	12.5	64	2.0
G	25	12.4	65	3.9
H	24	12.5	64	3.9
K	28	12.2	67	7.3
J	27	12.1	68	7.7
I	24	12.6	63	7.8
M	25	12.1	68	11.4
A	27	11.9	70	15.0 [a]
C	21	12.0	69	15.0 [a]
L	32	11.9	70	15.7
P	49	11.6	74	16.0
F	32	12.1	68	17.5
F*	36	12.1	68	17.5

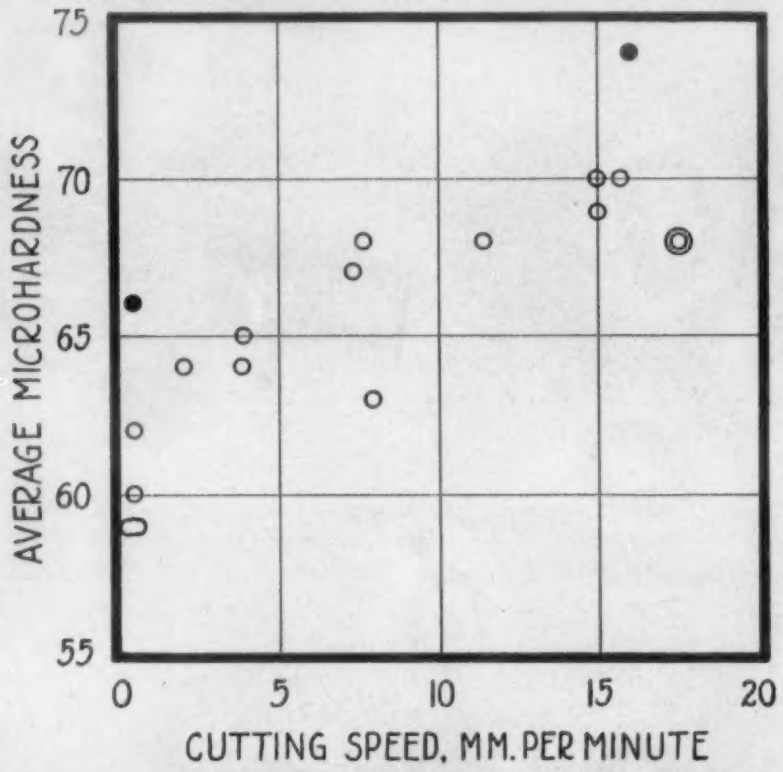
[a] Approximate.

Data

In the Table are given the microcut serial number, the number of readings of width along the microcut, the average width in microns, the average microhardness and the rate of cutting per minute. Four cuts were made using the motor drive at rates of 0.3 to 0.4 mm. per min. The average microhardnesses for these cuts were 59, 62, 59 and 60, respectively. Microcuts at approximately 2, 4, 8 and

12 mm. per min. gave average microhardnesses which tended to increase with increasing speed of cutting. Five cuts were made at 15 to 17.5 mm per min. with average microhardnesses of 70, 69, 70, 68 and 68, respectively. All the latter cuts were made by hand drive. Cuts O (0.4 mm. per min.) and P (16 mm. per min. in the Table) were made on a different part of the bar and probably indicate a true difference in gross hardness. The difference in microhardness, 66 to 74, is of the same order as is found with the other series of microcuts at comparable differences in cutting speed.

In this illustration, the average microhardness of each cut



The average microhardness of a pure silver bar is plotted against the speed of cutting. There is a fairly uniform increase of average microhardness with cutting speed. The black circles represent cuts O and P made on a different part of the bar.

is plotted (ordinate) against the cutting speed. A fairly uniform increase of microhardness with speed of cutting is indicated, although the results are scarcely concurrent enough to justify the assumption of a particular sort of increase, i.e. linear vs. logarithmic.

The difference between the average widths at cutting speeds of 0.4 and 16 mm. per min., is only 1 μ, corresponding to a microhardness difference of approximately 10 units at the widths measured. The lack of uniformity noted above is not serious since the differences in average widths at a given speed (for example, the four cuts at 0.4 mm. per min.) are of the order of 0.3 μ. The average deviation of the readings along a given cut is usually of the same order. Consequently, the difference in microhardness, 60 at 0.4 mm. per min. to 70 at 16 mm. per min., is probably statistically real.

Discussion

In the report of Sub-committee V on microhardness (1926) of the A.S.T.M.[3], the effects of cutting speed on the microhardness of 6 metals were summarized as follows: "The variations in width of cut appear to bear no very significant relation to the speed at which the cut was made." The two cutting speeds used were about 4 and 50 mm. per min. The slow speed is in the region used (see Table); the rapid is so much faster than any used (see Table) that it would seem, since no great differences were observed, that with increased speed a maximum "apparent" microhardness may be reached. More marked variations in microhardness might be expected comparing the results of very slow cutting, e.g. 0.1 mm. per min., with those of very rapid cutting.

In the same report[3], six observers, using 4 microcharacters, tested 11 different metals with the following result: "It will be noted ..... that the agreement..... is much better for the harder materials than for the softer ones." If the metals were cut at widely different speeds, this may have been one factor contributing to the wide range of microhardnesses found in the very soft materials.

In a personal communication, C. H. Bierbaum has commented that, in general, the wide range of microhardness found for a given metal or alloy is disappointing to those investigators who like to pigeon-hole in their minds a definite material with definite physical properties. "As the degree of refinement of testing hardness of a substance is increased, we find that a correspondingly wider range of hardness is found." He suggests that the wider range may be attributed to several factors, as follows: (a) the anisotropy of the crystals which have a different hardness when cut in different directions, (b) the hardness of the grain border, (c) the time factor involved in the flow of the metal, and (d) the limit of error of observation. In the data described in the Table, the results of the action of all of these factors are lumped, the time of cutting being the only variable.

If the "apparent" microhardness depends on the speed with which the cut is made, then for completeness either the approximate speed of cutting should be included with statements of the microhardness of ductile metals or a standard rate of cutting should be adopted. This standard rate might be determined in two ways: (a) by letting an arbitrary rate of so many mm. per minute be agreed upon regardless of the material, hard or soft, or (b) by letting a rate dependent on the properties of the material be fixed by the investigator's own study. The second alternative has already been proposed by C. H. Bierbaum[2] as follows: "The rate of travel should be so slow that no additional indentation is effected by stopping." By the adoption of such a rate, although it will vary from sample to sample, reproducible readings may be obtained. The mechanics of finding the exact spot along a microcut where the diamond was permitted to stop requires only the calibration of the mechanical stage scale and vernier in terms of the filar micrometer cross hair.

Summary

1. The "apparent" average microhardness of a material (for example, pure silver) may be affected by the speed of cutting, in this case, increasing with increasing speed.

2. This variation is due to the time factor involved in the flow of the metal or other material.

3. For very ductile metals, either the speed of cutting should be included with statements of the microhardness, or that standard rate of cutting should be adopted which produces no increased width of cut by stopping.

References

[1] H. C. Hodge and J. H. McKay. *Journal*, American Dental Association, Vol. 20, 1933, page 227.

[2] C. H. Bierbaum. *Chemical and Metallurgical Engineering*, Vol. 28, 1923, page 304; Report of Sub-Committee on Bearing Metals, *Mechanical Engineering*, Vol. 41, June 1919, page 537-538.

[3] H. S. Rawdon, Chairman Sub-Committee V of Committee E4, *Proceedings*, American Society of Testing Materials, Vol. 26, Part 1, 1926, page 573.

CONTROLLING A

"CONTROLLED ATMOSPHERE"—II

(Concluded from the February Issue)

by A. E. Krogh *Engineer, The Brown Instrument Co., Philadelphia*

Some Results of the Tests

Fig. 7 shows the relationships of CO_2, CO, CH_4, and H_2 found in the electric furnace when city gas feed was used. Some of the interesting points about these curves are:

1. Note the slope of the CO_2 curve at 1400 deg. F. and the changes in shape and slope which occurred as the furnace temperature was increased. It is easy to understand why CO_2 measurement by means of an Orsat at low air/gas ratios is so totally unsatisfactory. For example, at 1400 deg. F., a 100 per cent change in the air from a ratio of 1/1 to a ratio of 2/1 produced a change of only 0.4 per cent CO_2 (from 2.9 to 3.3). Since a good operator with a good Orsat will repeat readings within ± 0.2 per cent, it is obvious that CO_2 readings taken in this manner are quite meaningless under such conditions.
2. Similar comments apply for CO, though to a less degree. We are informed that our experience in finding measurable quantities of H_2 before CO becomes appreciable, checks the findings of many other observers.
3. The hydrogen curves are also very interesting. (The high range scale should be used in reading these.) Note the very large percentages of hydrogen found at low air/gas ratios, especially at the higher temperatures. It is evident that hydrogen, which does not later burn, is released from combination by cracking of the illuminants and CH_4 at the higher temperatures. On the other hand, at the lower temperature (1400 deg. F.), 43 per cent H_2 was put into the furnace. No air was added, yet the final atmosphere analysis gave only 36 per cent H_2. The CO and CO_2 percentages were high and probably the missing H_2 had combined with O_2 to form H_2O.
4. The curves marked CH_4 plus C_6H_6 represent the values found by absorption of CO_2 in the residual gas after combustion. The relative quantities of each are not definitely known. It is believed that the city gas feed ordinarily contained about 2½ per cent C_6H_6 and that the furnace atmosphere contained only traces. If such be the case, the curves actually represent CH_4.
   For equal air/gas ratios at 1600 deg. F., greater CH_4 percentages were obtained than at 1400 deg. At 1800 deg. these curves undergo a decided change in shape, while at 2200 and 2400 deg. the amount present diminishes very rapidly. It will be noted that at the higher temperatures the tops of the CH_4 curves are not brought to the 0 per cent point. This is because the results obtained in those ranges appeared extremely inconsistent, and we have not had an opportunity to recheck the values.
5. It will be remembered that the gases were cooled and passed through calcium chloride before measurement and, therefore, H_2O is not considered in these values. Thus the sum of the percentages shown when subtracted from 100 per cent should equal the per cent nitrogen present.

Fig. 8 shows similar data for Pyrofax gas feed. The following points appear to be particularly worth noting here:

A. The hydrogen present is always much less than when city gas is used. There is a decided change in the shape of the hydrogen curve somewhere around 2000 deg. Readers of this report have commented that a slight air leakage and consequent burning of some hydrogen to water vapor would account for this, since moisture was not determined.
B. The CO_2 obtained was much higher for Pyrofax than for city gas under equal CO conditions.
C. The CO and CH_4 curves are superficially quite similar to those obtained by city gas feed.

It will be noted that oxygen and illuminants are not shown on the curves. This is because our chemical apparatus was hardly reliable for the very small percentages found in all instances of incomplete combustion.

It must be remembered that the catalytic effect of iron, i.e., of the work being heat treated, is absent in these tests and that the gas composition will be somewhat altered by such catalytic effects. However, since those effects will vary with particular steels, the base line for their study has to be the relations that exist without such catalysts. It should also be remembered that no removal of water vapor was made before the gas entered the furnace proper, and that the gas reactions in the presence and in the absence of water vapor will not always be the same.

Discussion of Results

Having secured the data shown in Figs. 6 and 7, we may now consider the characteristics resulting from these relationships, remembering that our purpose is to determine the most significant measurable property of furnace atmospheres. Referring to H. W. Gillett's correlated abstract in the August, September, October, and November, 1935, issues of METALS AND ALLOYS, we find the statement:

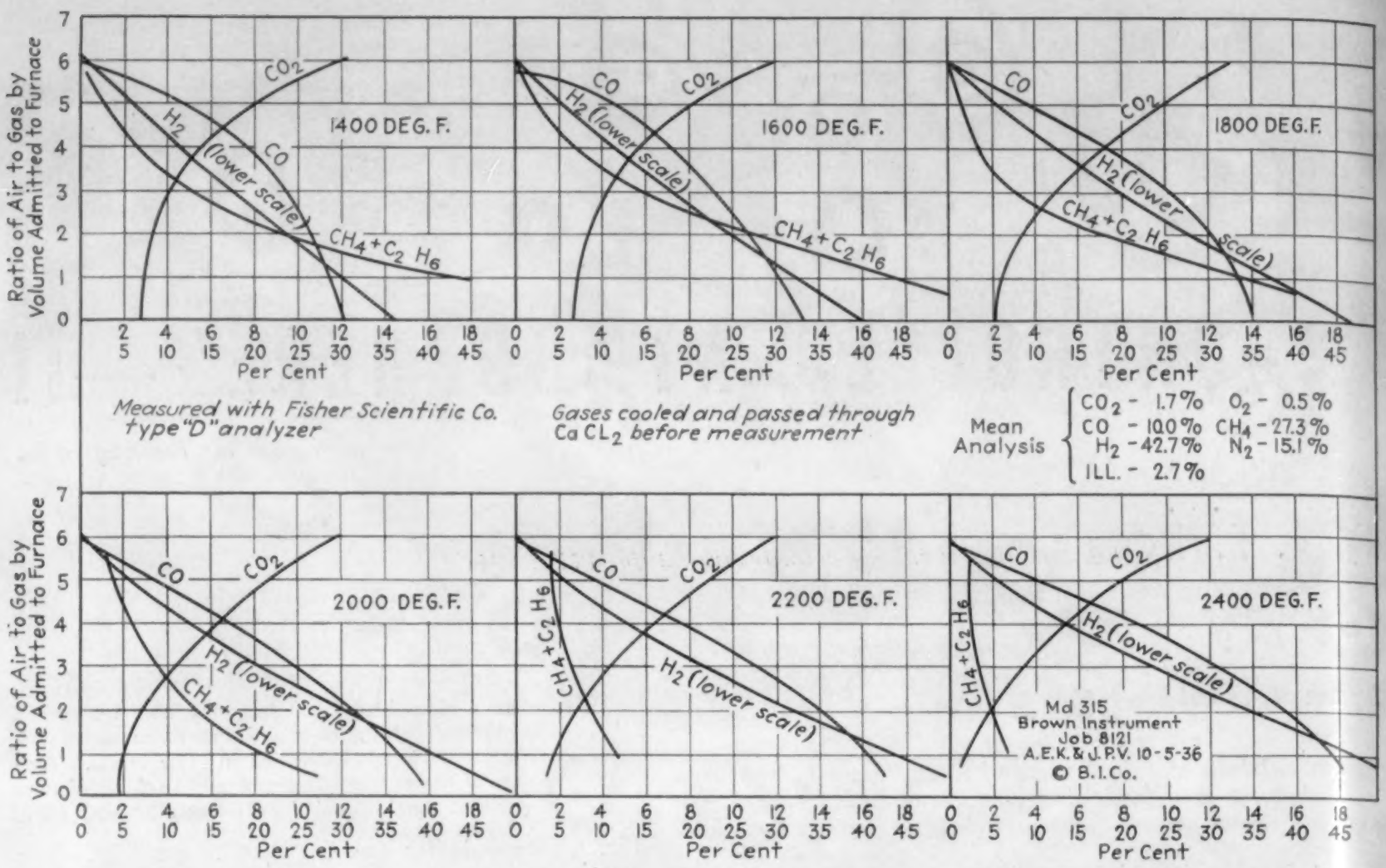


Fig. 7—Relation of Gases in Atmospheres of C. I. Hayes "Certain-Curtain" Furnace Using Providence City Gas Feed.

For the reactions of the pairs of gases CO and CO_2; H_2O and H_2; CH_4 and H_2; in contact with austenite saturated with carbon at different temperatures, above A_1, or with ferrite below A_1, the equilibria have been worked out with fair agreement among different workers and are conveniently summarized by Stansel (N. R. Stansel, "Industrial Electric Heating"—J. Wiley & Sons, New York). These (data) are for stagnant, equilibrium, conditions and the behavior will be modified if a gas not originally in equilibrium with the steel at a given temperature is passed over the steel, the behavior being affected by the rate of flow. . . .

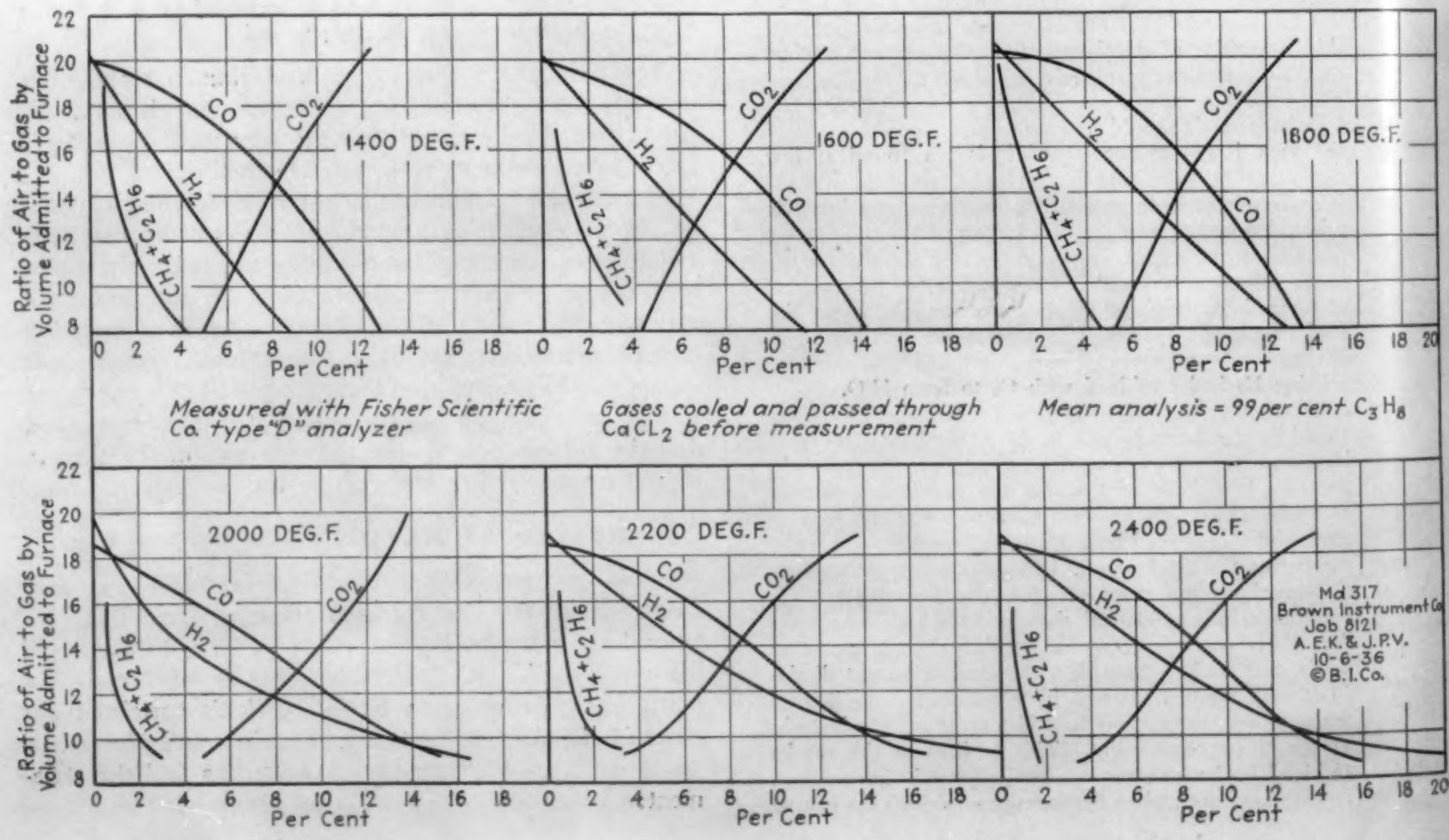


Fig. 8—Relation of Gases in Atmospheres of C. I. Hayes "Certain-Curtain" Furnace Using Pyrofax Gas Feed.

In view of this, we have taken the data secured experimentally and plotted Fig. 9 which shows the ratios of CO_2/CO and CH_4/H_2 for the two gases used in our tests in the electric furnace. On these curves we have also superimposed Stansel's equilibrium data. These ratio curves are plotted on semi-logarithmic cross section sheets because it is felt that per cent changes in values are of greater significance than absolute changes when equilibria are under consideration. It is interesting to note that Stansel's values, when plotted on semi-logarithmic paper, show nearly straight lines.

It must here be emphasized that the data quoted apply only to equilibria with the carbon in the particular steel specified. A steel of some other carbon content or containing other metals will not conform to the particular values shown.

It will immediately be observed that in our tests (down to 1400 deg. F.), the equilibrium value for CH_4/H_2 was not reached at any time and was only barely reached in the case of CO_2/CO when city gas was used. On the other hand, it is known that "good steel" can be and is being produced with the atmospheres illustrated, so the reason presumably lies in the fact that the influence of CO_2/CO appears to be always decarburizing while that of CH_4/H_2 appears always to be carburizing. If the two influences are equal, opposite, and simultaneous, it seems reasonable to assume that the atmosphere will effectively be neutral from a carburizing standpoint.

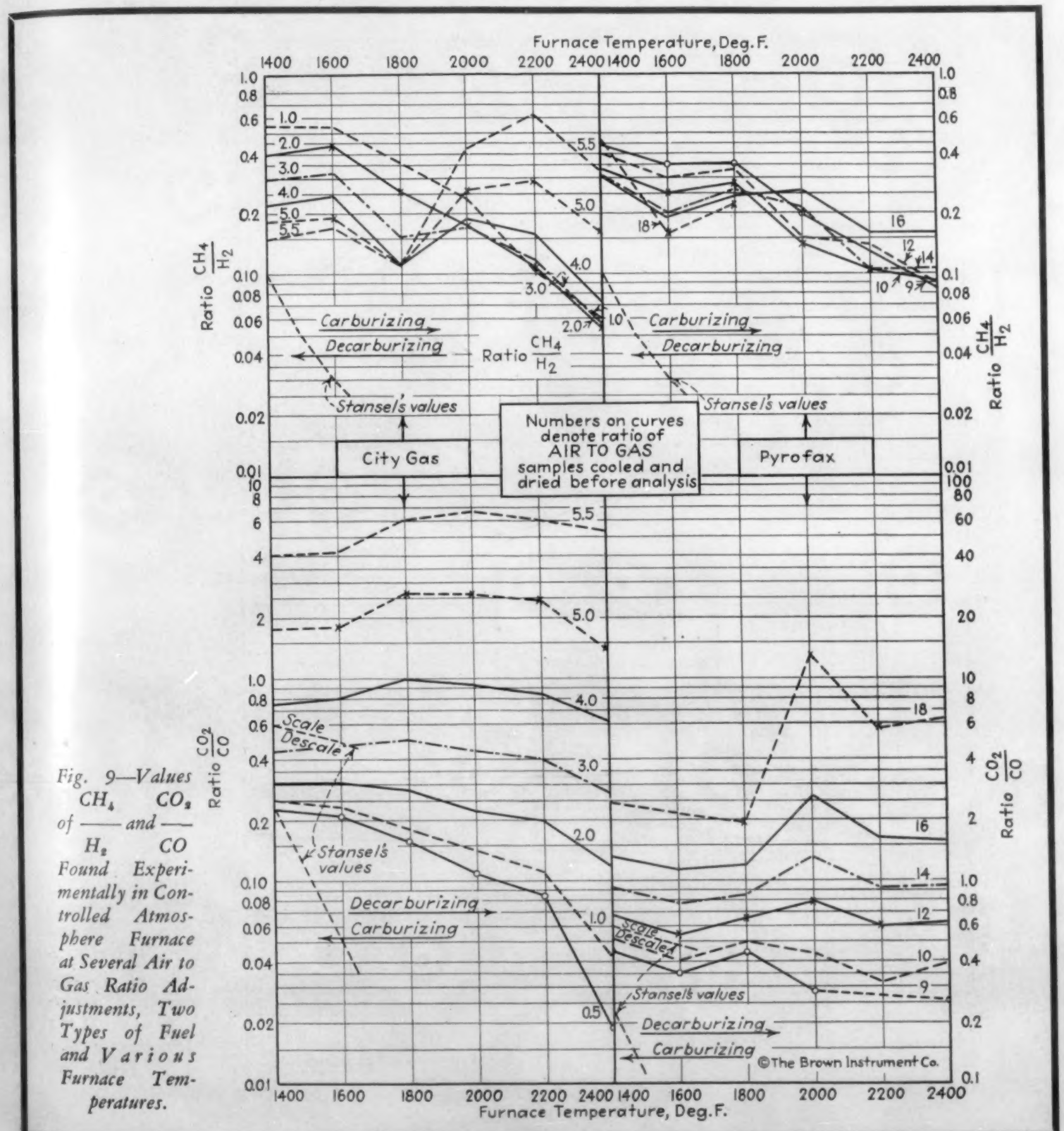


Fig. 9—Values of $\frac{CH_4}{H_2}$ and $\frac{CO_2}{CO}$ Found Experimentally in Controlled Atmosphere Furnace at Several Air to Gas Ratio Adjustments, Two Types of Fuel and Various Furnace Temperatures.

When we try to apply similar logic with respect to scaling, we find that CO_2/CO may oxidize or deoxidize, depending upon the air/gas ratio in any particular instance. Unfortunately, our lack of test data in respect to water vapor renders it impossible to show the complete picture in regard to scaling, but it appears reasonable to assume that a similar balance is established in this case. In fact, quoting from Dr. Gillett's paper, referred to above:

> As far as mere scaling goes, the effect of H_2, H_2O, CO, and CO_2 mixtures can be deduced from the $CO:CO_2$ ratio alone, since the total equilibrium is expressed by the ratio
>
> $$\frac{(H_2O)\quad(CO)}{(H_2)\quad(CO_2)}$$
>
> of the water-gas constant, so if a non-scaling $CO:CO_2$ ratio is chosen, the $H_2O:H_2$ ratio in equilibrium with it will also be non-scaling. But this does not hold for decarburization.

The converse is probably also true so that if a non-scaling H_2O/H_2 ratio be found, the CO_2/CO in equilibrium with it will also be non-scaling.

Referring then to the carburizing factors, we set up a similar ratio:

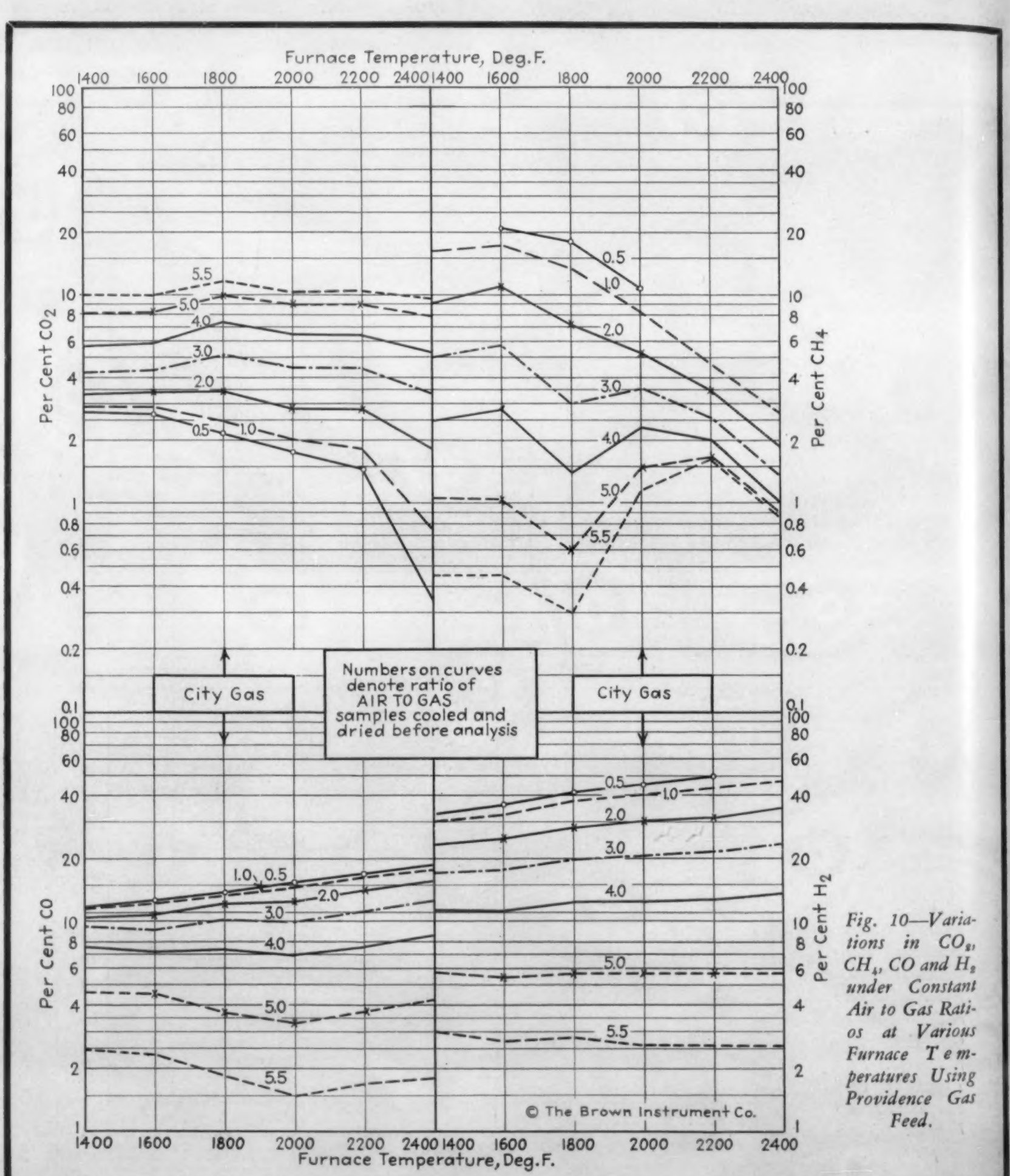


Fig. 10—Variations in CO_2, CH_4, CO and H_2 under Constant Air to Gas Ratios at Various Furnace Temperatures Using Providence Gas Feed.

$$\frac{(CH_4)\quad(CO)}{(H_2)\quad(CO_2)}$$

The striking thing about these scaling and carburizing ratios is that

$$\frac{(CO)}{(H_2)\quad(CO_2)}$$

is common to both.

In order to select the gas of greatest significance in this factor, the curves in Figs. 10 and 11 have been plotted on semi-logarithmic cross section paper. Referring first to the data for Providence City Gas, Fig. 10, we find:

1. CO_2, CO, and H_2 all change reasonably smoothly with temperature for a given air/gas adjustment. CH_4 is much less regular.
2. Of the three gases common to both the scaling and the decarburizing ratios, hydrogen is found in much greater quantities than the other gases.

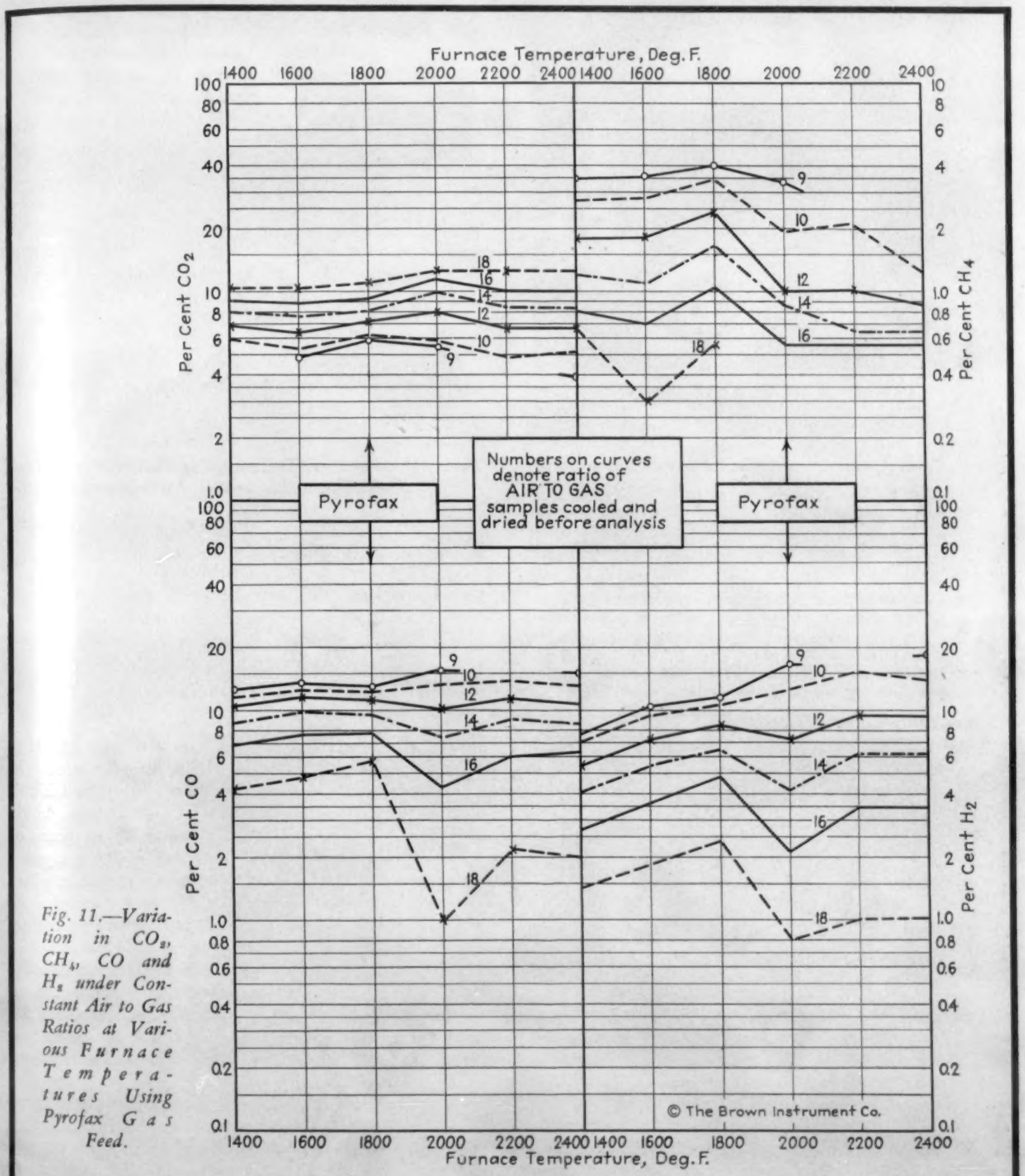

Furnace Temperature, Deg. F.
1400 1600 1800 2000 2200 2400
Per Cent CO2
Per Cent CH4
Per Cent CO
Per Cent H2
Pyrofax
Pyrofax
Numbers on curves denote ratio of AIR TO GAS samples cooled and dried before analysis
© The Brown Instrument Co.
Furnace Temperature, Deg. F.

Fig. 11.—Variation in CO_2, CH_4, CO and H_2 under Constant Air to Gas Ratios at Various Furnace Temperatures Using Pyrofax Gas Feed.

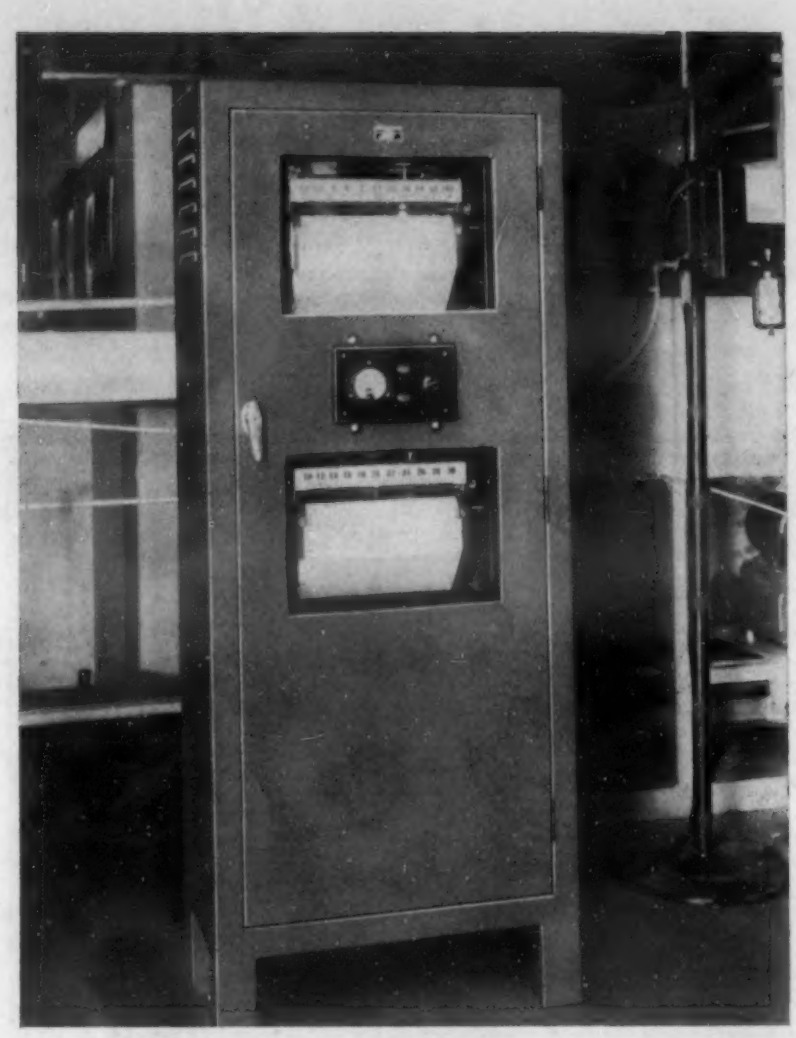


Fig. 12—Analy-Graph and Temperature Controller Mounted in Ventilated Metal Cabinet for Complete Furnace Control.

3. Hydrogen and carbon monoxide tend to vary together, though not exactly so.

Transferring our attention to Fig. 11, we similarly find that for Pyrofax gas:

1. CO_2 varies little as furnace temperature changes for given air/gas ratios. Conversely, little variation is also shown at any given temperature as air/gas ratio changes. This is not so for the other gases.
2. Hydrogen and carbon monoxide again tend to vary together, though not exactly so.

Summarizing the various points:

1. The factor $\frac{CO}{(H_2)\quad(CO_2)}$ is common to both the scaling and the carburizing ratios.
2. The ratios $\frac{(CO)}{(CO_2)}$ or $\frac{(CO_2)}{(CO)}$ can be more easily deduced from the air/gas ratio than can hydrogen.
3. CO_2 varies little with furnace temperature changes.
4. CO is more irregular.
5. H_2 is present in greatest quantities and varies most. It is, therefore, the most sensitive indicator of changing conditions.

Conclusions

The tests herein described were undertaken in the hope that a meter could be developed to meet the very obvious need for a graphic record of what we may, for want of a better term, call the "quality" of furnace atmospheres. We have concluded that such a meter should be particularly sensitive to hydrogen in atmospheres resulting from partial combustion and to oxygen or carbon dioxide when combustion has been complete.

Hydrogen differs greatly from other gases in several physical properties. We have found thermal conductivity one which was reliable and relatively easy to measure. In Table II are listed the relative thermal conductivities of a number of different gases. It is apparent that hydrogen is outstanding in this respect. Similarly, where combustion is complete and only O_2, N_2, and CO_2 appear in the dried gas, CO_2 differs considerably from its fellows.

We have, therefore, concluded that a thermal conductivity method would offer the best means upon which to base continuous automatic measurement of furnace atmosphere quality. The Furnace Atmosphere Analy-Graph is the result. In order to render the instrument of maximum usefulness, an electrical circuit has been devised such that all types of furnace atmospheres may be measured upon it, whether resulting from complete or incomplete combustion or from dissociation. The type of chart produced is illustrated in Fig. 6. [See Part I, February Issue.]

Simultaneously with the tests described, two such meters were used in production tests on furnaces of the design shown in Fig. 1 at other plants. In addition, considerable production data have since been secured from the electric furnace with the meter used in the tests. The results have been most gratifying. We have substantial proof that the measurement of thermal conductivity is valuable, and that the Analy-Graph is of great assistance to heat treaters in actual production work.

Obviously it is not necessarily a cure-all to hold the hydrogen, and by that token, the other constituents constant, for if the use is one for which water vapor should be removed, and its removal is not consistent, the H_2/H_2O ratio changes even though the H_2 be held the same. In such a case operators would, however, find it very difficult to maintain a given hydrogen content and attention would thus be drawn to the difficulty. Some additional means of checking the uniformity of dehydration of the gas going to the furnace proper would then be very desirable. Nor does the instrument tell the operator what particular atmosphere is best for a new steel or a different temperature of heat treatment.

Table II.—Relative Thermal Conductivities of Some Gases Found in Furnace Atmospheres

Gas	Relative Thermal Conductivity (Air = 1) (at 32 deg. F.)	(at 212 deg. F.)
Oxygen	1.007	1.032
Nitrogen	1.003	0.998
Hydrogen	6.99	6.94
Carbon monoxide	0.927	0.924
Carbon dioxide	0.586	0.690
Sulphur dioxide	0.344	....
Methane	1.32	1.72
Ethane	0.875	1.09
Ethers, alcohols and illuminants	about 0.5	....

However, it does help him, once he has determined what atmosphere is desired, to secure the same atmosphere on another day. As a fund of information is secured, the Analy-Graph becomes increasingly valuable and helps heat treaters to meet the more and more rigid specifications encountered nowadays.

In closing, we wish to express appreciation to the many furnace manufacturers, heat treaters, metallurgists, and other engineers who have cooperated and given us much encouragement in the experimental work and subsequent interpretation of the results.

THE MANUFACTURE OF

VALVE SEAT INSERTS

FOR FORD ENGINES

by Edwin F. Cone

ONE OF THE IMPORTANT and interesting metallurgical developments of quite recent years has been the production of an unusual type of steel castings for automobile engines by the Ford Motor Co. They are characterized by a uniqueness in composition, so far as the balancing of the elements is concerned, and by special advantages as to cost of production.

It has been the good fortune of METALS AND ALLOYS to have had the privilege of describing the metallurgical story of several of these cast products—the crankshafts[1], the pistons[2], and the camshafts[3]—the first two being designated by Ford metallurgists as steel castings having high carbon content with substantial percentages of copper and varying quantities of other elements.

In this brief article there will be presented the metallurgical story of the manufacturing of Ford valve seat inserts—a small but important gadget in the successful operation of the V-8, or any automobile, engine.

Valve Seat Inserts

The valve seat insert is a small ring of metal—in the Ford car it is a casting or ring of steel about 1/4 in. thick and 1 5/8 in. in outside diameter. In the majority of automobiles this casting is made of gray iron, rather high in alloying elements including molybdenum, chromium and often tungsten, the total carbon content being about 3 per cent.

The conditions which valve seat inserts must meet are severe. The metal must be hard enough to resist the constant pounding of the valve, and it must be heat and corrosion resistant enough to prevent pitting and oxidation—caused by the hot exhaust gases of combustion. These reach about 1400 deg. F. at the surface of the valve seat, dissipating rapidly.

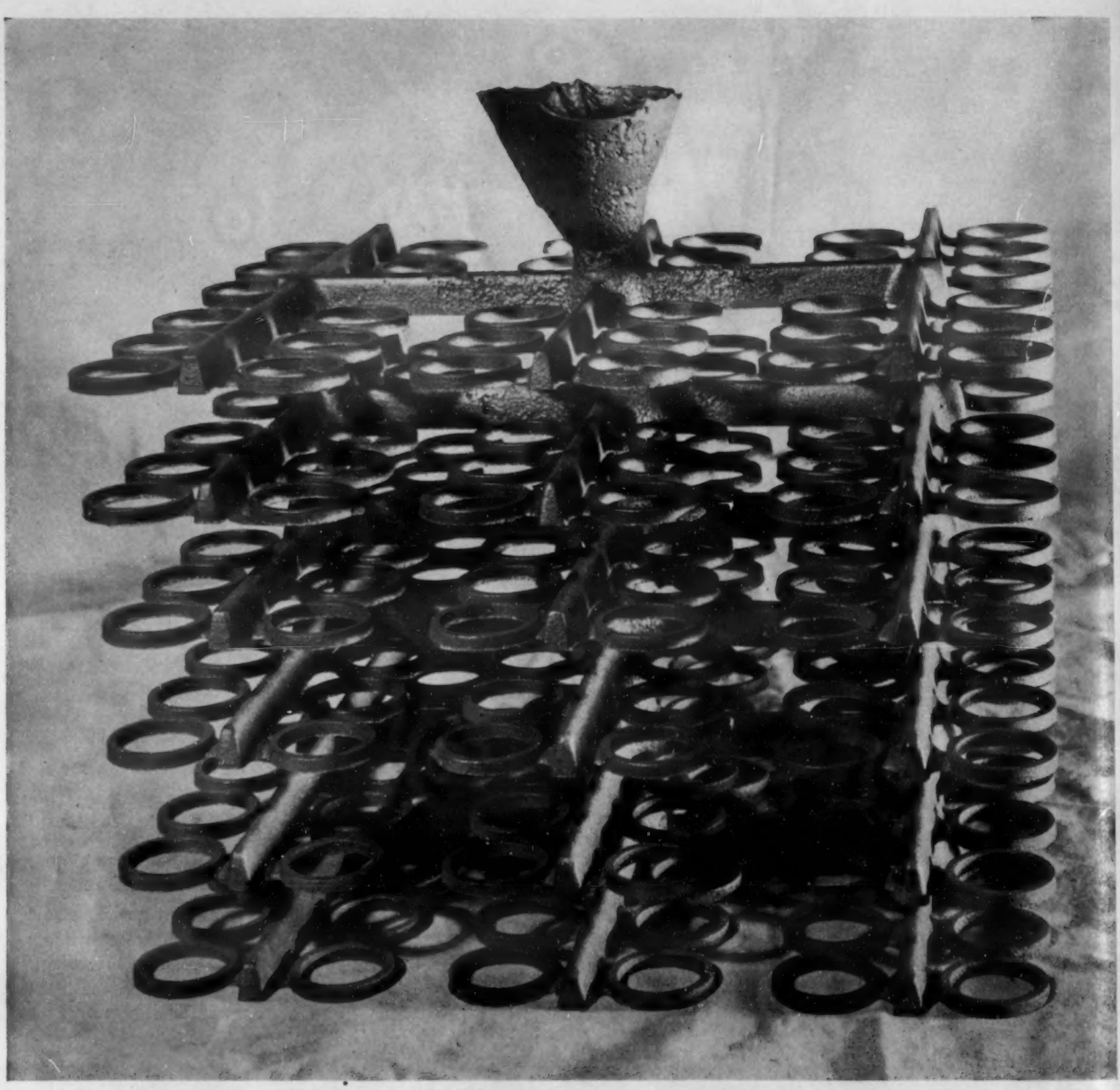
The metal in this casting must also have a coefficient of linear expansion approximately equal to that of the cylinder block. It also must possess a rather high elastic limit when hot—so as to prevent permanent deformation from the heat of the motor, developed during operation.

Alloy Gray Iron Valve Seats

Ordinary gray iron will meet the requirements of proper and correct linear expansion. Without the incorporation of the rather expensive alloys in the iron, however, the required hardness and heat and corrosion resistance cannot be obtained. In addition, the iron valve seat inserts have to be hardened and ground after machining. Their required physical properties depend on their being very hard—around Rockwell C 55 to 60.

Instead of using a high alloy gray iron in the valve seat inserts, the Ford company decided to employ re-melt, or scrap, high-speed steel from which to manufacture them. The supply of this from the large operations in the plant is usually ample. A metal of this nature, it was argued,

Pouring a Heat of Special Alloy Steel for Valve Seat Inserts.



The Group of 216 Valve Seat Inserts for Ford Engines as They Appear After Casting and Sand Removal.

could be run at a lower hardness—Rockwell C 40 to 46. This would be machinable and no extra hardening would be necessary. In other words, a composition of this nature would be rather soft for a valve seat insert and still possess the necessary physical properties because of its high tungsten content.

It must be understood that these inserts are not anchored in by a screw or by threads or by any similar means. They are shrunk in with the use of liquid air and depend entirely on their linear expansion and high elastic limit to hold them in position.

Composition of Ford Inserts

By using a charge of 100 per cent re-melt high-speed steel scrap, a satisfactory metal was obtained. The tungsten is held to a minimum of 14 per cent—somewhat lower than in the original scrap, due to melting losses and some dilution of the bath with ferrochromium and pig iron. The steel in the valve seat inserts, as a result of this practice, has approximately the following composition:

	Per Cent
Carbon	1.20 to 1.40
Manganese	0.30 to 0.50
Chromium	2.50 to 3.50
Silicon	0.30 to 0.60
Copper	1.50 to 2.00
Tungsten	14.0 to 17.0

The copper is obtained by adding scrap copper to the charge. As cast, this metal has a hardness of Rockwell C 50 to 60.

The Heat Treatment Used

The heat treatment to which it is now subjected is as follows:

Heat to 1450 deg. F., for 30 min. Cool at the rate of

125 deg. per hr. to 1000 deg. F. This will result in a hardness of Rockwell C 40 to 46.

This treatment is carried out in electric heat-treating furnaces and the castings are packed in heat-resisting nickel-chromium boxes to insure an even cooling.

This casting, after heat treatment, can be tool machined where necessary and finish ground without any further hardening treatment. It is then ready for use, after suitable cleaning by shot blast.

Melting and Foundry Practice

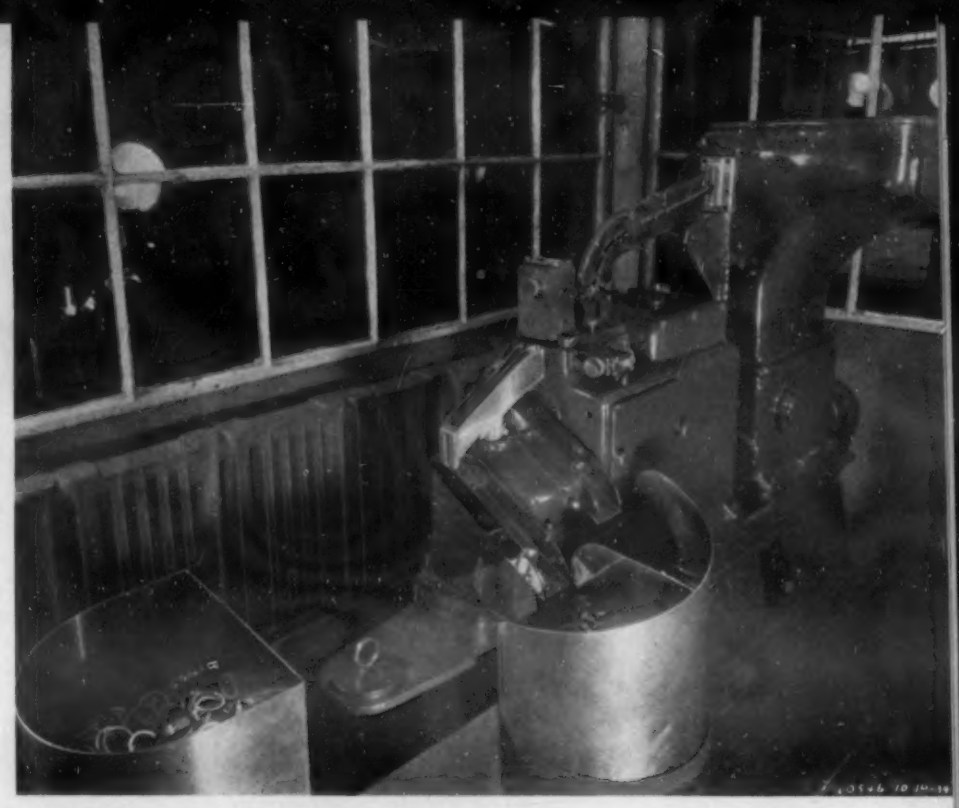
This alloy is melted in electric arc furnaces—about 500 lb. capacity—on an acid bottom, using, as indicated before, scrap high-speed drills or drillings—any high-speed scrap, even down to grindings from grinding wheels. Some pig iron and ferrochromium are also added.

This molten metal is poured in green sand molds, 36 inserts being molded in one plate or slab. These slabs or plates are stacked one on top of another in six layers so that 216 castings are cast in one pouring as shown by one of the illustrations.

From the analysis of this material as recorded above, it might be inferred that it would be difficult to cast. This is not the case. The carbon has been raised high enough to bestow excellent casting properties but not high enough to cause excess brittleness. The tungsten content insures a high elastic limit to the metal while hot.

Novel Machine for Inspecting Inserts

Every valve seat insert has to undergo a careful inspection. A novel machine has been perfected for this purpose. It inspects each casting for outside diameter, thickness, and for cracks. The castings are run through the machine, as illustrated, those imperfect in thickness or outside diameter falling through the two respective troughs. Castings in which a slight crack is present, when they fall on the round steel block in front of the machine, will not bounce into the receptacle but will fall down into the bottom of the machine.



The Special Testing Apparatus for Inspecting the Finished Valve Seat Inserts for Variations in Thickness, Diameter and Soundness.

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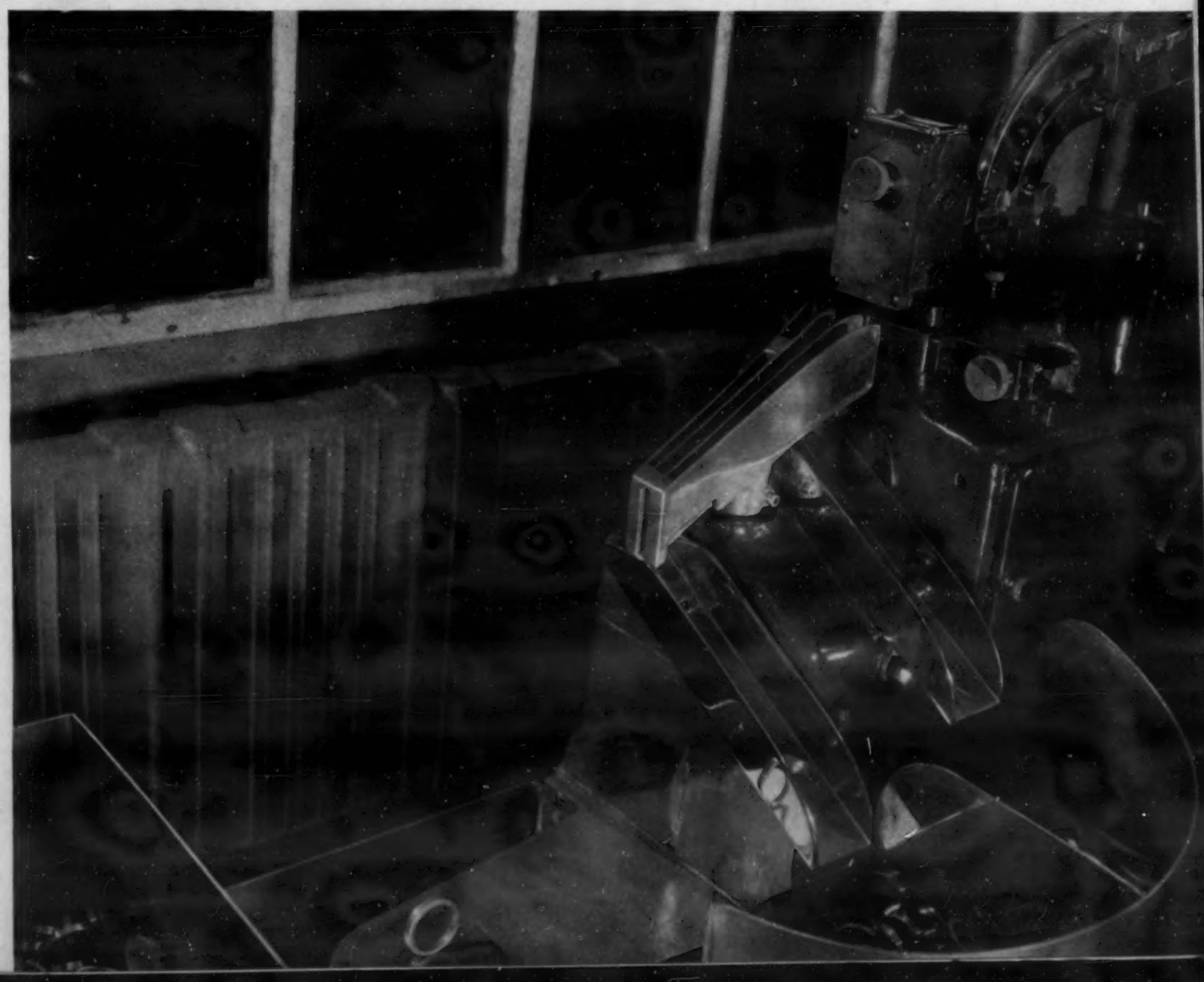
[1] "The Story of the Ford Cast Crankshaft", METALS AND ALLOYS, Vol. 6, Oct. 1935, pages 259-263.

[2] "The Lincoln-Zephyr Cast Alloy Piston", METALS AND ALLOYS, Vol. 7, Apr. 1936, pages 85-87.

[3] "Manufacture of Ford Camshafts", METALS AND ALLOYS, Vol. 7, Nov. 1936, pages 275-277.



A Close-Up of the Special Testing Machine.

Courtesy: Whiting Corp., Harvey, Ill.

Tapping a Brackelsberg Furnace in a Large American Foundry

NOMOGRAMS IN A PIPE FOUNDRY

by C. K. Donoho

Metallurgist, American Cast Iron Pipe Co., Birmingham, Ala.

THE NOMOGRAM, OR ALIGNMENT CHART, has been the subject of several interesting articles in the recent technical literature[1, 2]. A useful method for rapid graphical solution of routine calculations, the nomogram is now receiving the attention of engineers and scientists which it has long deserved.

However, probably the best use of such a rapid calculating method will be found among the practical men, especially in those cases where, in the rush of production, the foreman or superintendent must now waste a half hour every now and then getting out his log tables and slide rule to solve a problem of volume or weight which an unusual order has brought up. In most foundries, as in other industries, there are continually arising mathematical problems of two or three general types which though easily solvable by arithmetic or algebra, often cause delay and some tearing of hair on the part of the foreman.

This article attempts to explain simply the general principles of common types of nomograms, and to give a few practical examples which have been found to be of convenience at the foundry in which the author is employed.

Principle of the Nomogram

The cardinal principle of the nomogram is: Any equation whose locus is a straight line when plotted on rectangular coordinates, has for its locus a point when plotted on the coordinates of the nomogram. (Nomogram, as used here, refers to the simplest type of alignment chart consisting of parallel axes with a center scale of values sought.)

An example will demonstrate this clearly: In the equation

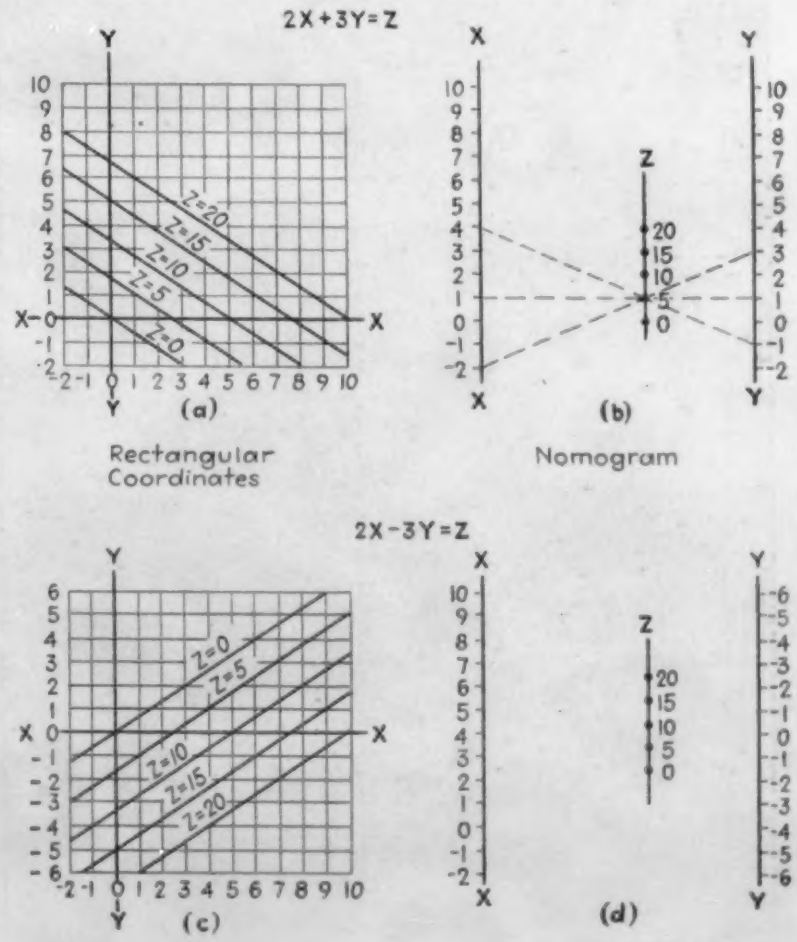
$$2X + 3Y = Z$$

X and Y are determined and Z is to be calculated. When Z is 0, 5, 10, 15, the loci of the equations thus formed when plotted on rectangular coordinates, are a series of parallel straight lines Fig. 1 (a). Plotted on nomographic coordinates, Fig. 1 (b), there is a point corresponding to each linear locus on rectangular coordinates. For example, lines connecting all values of X and Y which give $Z = 5$ cross at one point between the X and Y axes.

It will be seen, Fig. 1 (b), that the point loci of the equations for different values of Z fall on a straight line parallel to the two axes, and in such position that the distances from the center Z axis to the X and Y axes are in the ratio of 3 to 2, respectively. The position and graduation of the Z scale are determined by the type of equation and the coefficients of the variables. Formulae exist for locating and dividing the center scale in most types of nomograms[1, 2], but it is often simpler to locate the necessary point loci by plotting on a layout.

When other desired values of Z are calculated and marked on the center scale we have the simplest type of nomogram. With X and Y known, to find Z, merely connect the values of X and Y with a straight edge and

Fig. 1.—Plotted on Nomographic Coordinates.



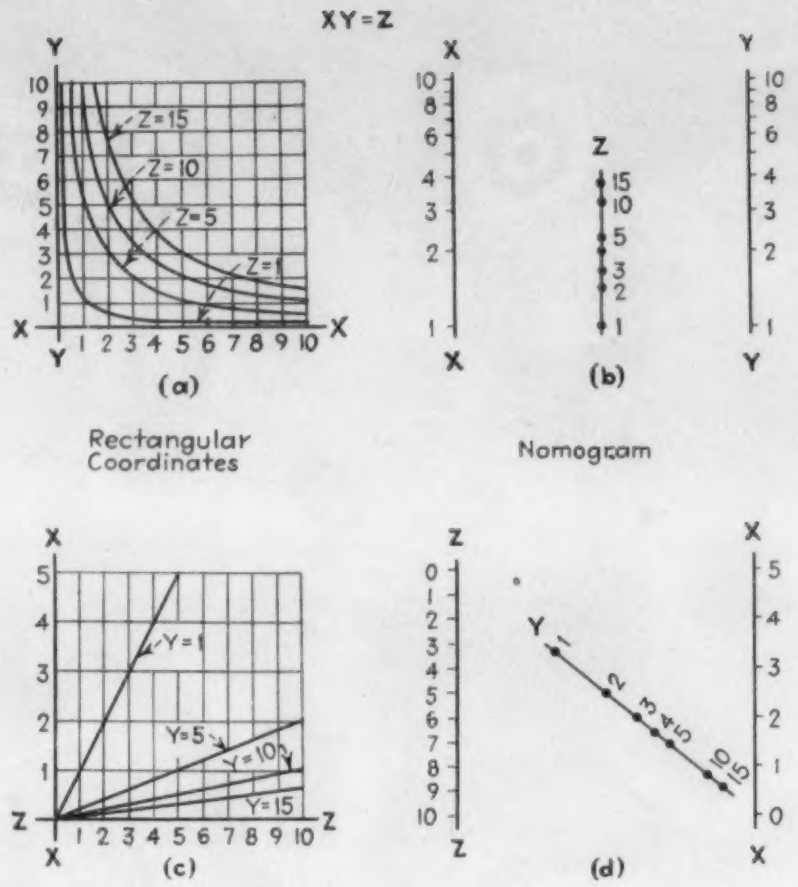
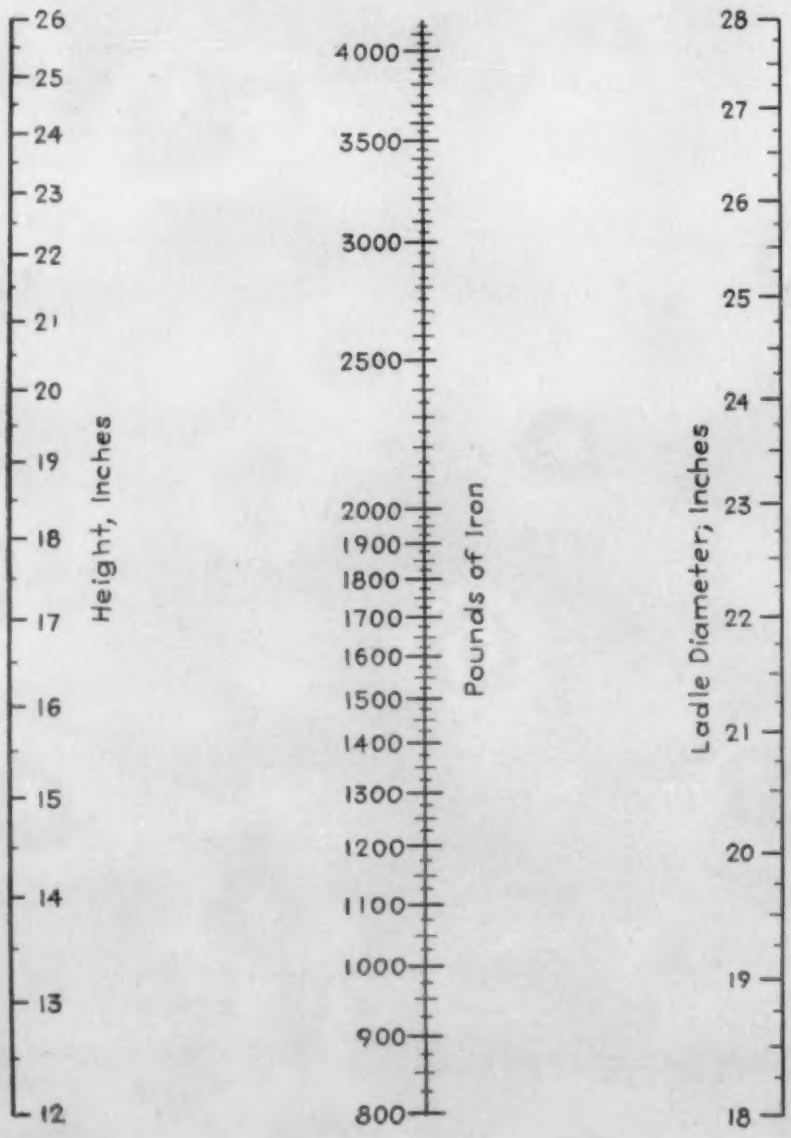


Fig. 2.—A Special Type of Hyperbola.

Fig. 3.—Nomogram for Calculating Ladle Capacity.



read the value of Z on the Z scale. Fig. 1 (c) and (d) show the similar treatment of the equation

$$2X - 3Y = Z$$

When this equation is plotted as a nomogram, Fig. 1 (d), note that the X and Y scales must ascend in opposite directions, because of the negative sign.

However, the simple linear equations of this type are so easily solved that there is rarely any need for constructing a nomogram for this type of problem. By proper choice of scales and simplification of the equations, many more complex equations become linear on rectangular coordinates, and may be set up in the form of a nomogram with equal facility.

Equations of the type $XY = Z$ (a special case of the hyperbola) Fig. 2 (a), become linear when plotted on log scales, as the equation then becomes, in effect, Log X + Log Y = Log Z, which is a linear equation. This type of equation may be plotted as a nomogram by the use of log scales for the X and Y axes, and the Z line between will also be a log scale, Fig. 2 (b).

A way of constructing a nomogram for this type of equation without the use of the log scales is to make the X or Y values the middle scale. For example, for any constant value of Y, the equation is linear in X and Z, Fig. 2 (c), and on nomographic axes, all values of X and Z which give a certain value of Y will cross in a point, Fig. 2 (d).

It must be remembered, however, that a nomogram cannot be constructed without the use of log scales with Z as the middle axis, because with Z constant the equation is not linear in X and Y.

Equations of the type:

$$X = YZ^2 + Z$$

are best handled by making X and Y uniform outside scales and plotting the points for the Z scale in the middle.

An exponential function: $X = Y^z$ becomes linear in X and Y on log scales since:

$$\text{Log } X = Z \text{ Log } Y$$

An equation:

$$X = Z^y$$

becomes linear in X and Y when plotted with a log scale for X values and a uniform scale for Y values since: Log X = Y Log Z.

A complex equation of the type:

$$2X = Y^2Z + Z^2X + Z$$

becomes linear in X and Y and when the X axis is a uniform scale and Y axis is a squared scale.

These particular examples given are by no means meant to be complete but are given in order to illustrate the principle that scales must be so chosen that the equation becomes linear on rectangular coordinates, before a nomogram of the type here considered can be constructed. Equations of only three variables are considered here, but by double axes or "box" nomograms equations of four or more variables may be solved by the same general principles[2, 3].

Calculating Weight of Iron in Ladle

At the American Cast Iron Pipe Co. it is often necessary to put a certain weight of iron in a ladle. Since the diameters of the ladles vary, not only with different ladles, but

also with each new lining, calculations were often required to determine the necessary height in the ladle to give the desired weight of molten iron. While this calculation is not arduous, it was a decided bother to the man on production to stop and figure a ladle every other day. Also, a costly mistake is very easy to make, as in the rush of production such a calculation may easily go awry.

The equation to give the height (inches) in a cylindrical ladle of given diameter (inches) to give a certain weight (pounds) of iron is:

$$\text{Height} \frac{4 \times \text{Wt}}{\pi\ (\text{Dia})^2 \times 0.26}$$

Where 0.26 is the weight in pounds of a cubic inch of the molten iron used.

Log scales were used to make the equation linear, and the completed nomogram is shown in Fig. 3. Prints of this chart are posted in the shop where needed, and the workman simply measures the diameter of his ladle, and with a straight edge connecting this figure to the desired weight reads the necessary height on the scale for height. It need hardly be said that the use of this nomogram has effected time saving, greater accuracy, and the elimination of costly errors.

Another simple calculation which may be made rapidly on the job by the use of a nomogram is shown in Fig. 4. This chart calculates the percentage of two irons of different silicon contents to be used to give a desired silicon content somewhere between the two.

Suppose it is desired to figure a mix averaging 1.75 per cent silicon from scrap of 1.50 per cent silicon and pig iron of 2.25 per cent silicon. With a straight edge connect 1.75 — 1.50 = 0.25 on the left hand scale to 2.25 — 1.75 = 0.50 on the right hand scale and read on the middle scale — 67 per cent of the 1.50 per cent Si scrap and 33 per cent of the 2.25 per cent Si pig must be used.

Figuring a Mixture

As another example, suppose it is desired to figure a mix of 1.80 per cent silicon using 25 per cent of a 1.50 per cent silicon return scrap and two pig irons of 1.75 and 2.25 per cent silicon. Connect 1.80 — 1.50 = 0.30 on the left hand scale to 25 per cent on the left side of the center scale and read on the right hand scale. The reading is 0.10. Therefore, the pig irons used with the scrap must average 1.80 + 0.10 or 1.90 per cent silicon. The percentages of the two pig irons to be used are found, as in the first example, by connecting 1.90 — 1.75 = 0.15 to 2.25 — 1.90 = 0.35 and reading the center scale. The reading gives approximately 70 per cent of the low silicon pig iron and 30 per cent of the high silicon pig iron. Therefore, for a mix of 1.80 per cent silicon, 25 per cent of 1.50 per cent silicon scrap is added to a mixture of pig irons which is 30 per cent of the 2.25 per cent silicon pig iron and 70 per cent of the 1.75 per cent silicon pig iron, or the final mix is:

1.50% Si scrap, 25%; 2.25% Si pig, 22.5%; and 1.75% Si pig 52.5%.

If three pig irons in addition to the scrap are to be used, by choosing a definite percentage of one, the average silicon content of the other two is determined and finally the percentages of these two are found as before.

This chart is shown mainly to illustrate another general type of problem easily solved by the nomogram. The

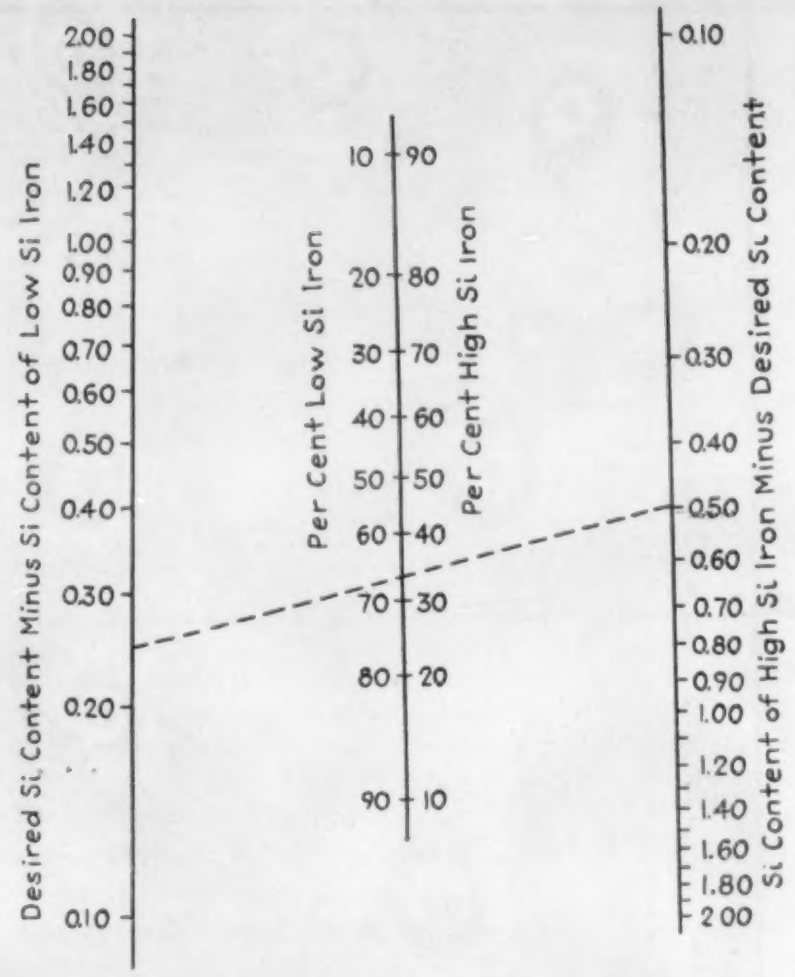
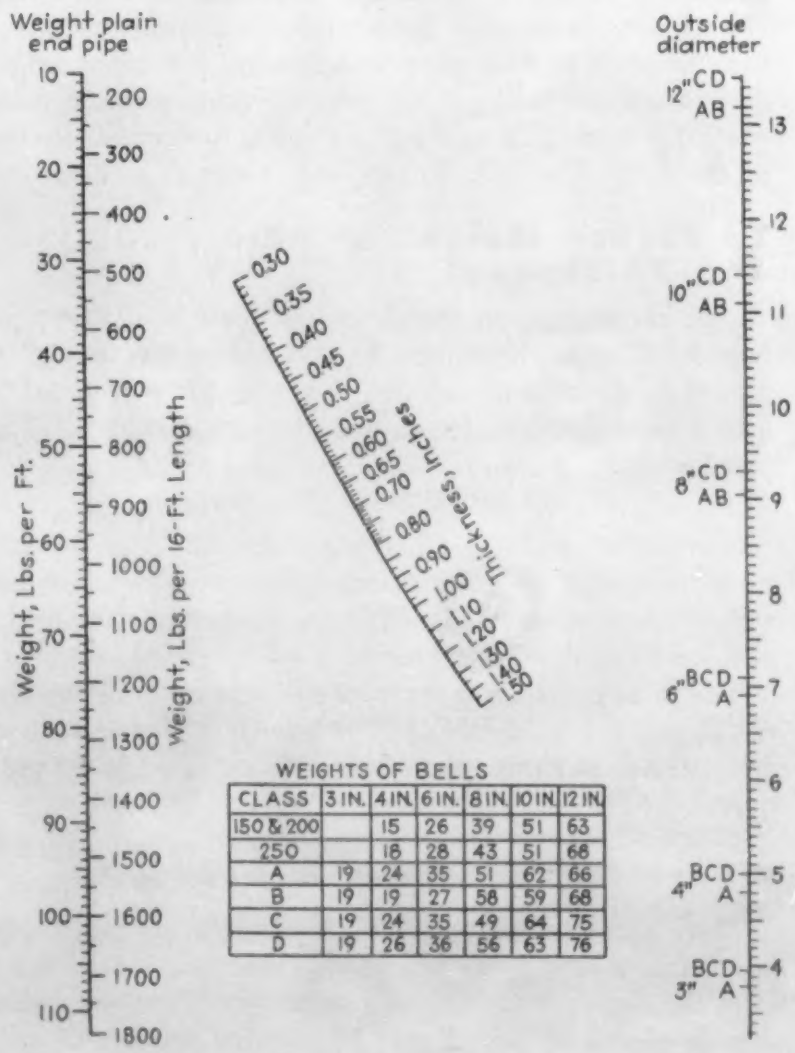


Fig. 4.—Calculating the Percentage of Two Irons of Different Silicon Content to Give a Desired Silicon Content.

Fig. 5.—Weight-Thickness-Diameter Nomogram for Cast Iron Pipe.



WEIGHTS OF BELLS

CLASS	3 IN.	4 IN.	6 IN.	8 IN.	10 IN.	12 IN.
150 & 200		15	26	39	51	63
250		16	28	43	51	68
A	19	24	35	51	62	66
B	19	19	27	58	59	68
C	19	24	35	49	64	75
D	19	26	36	56	63	76

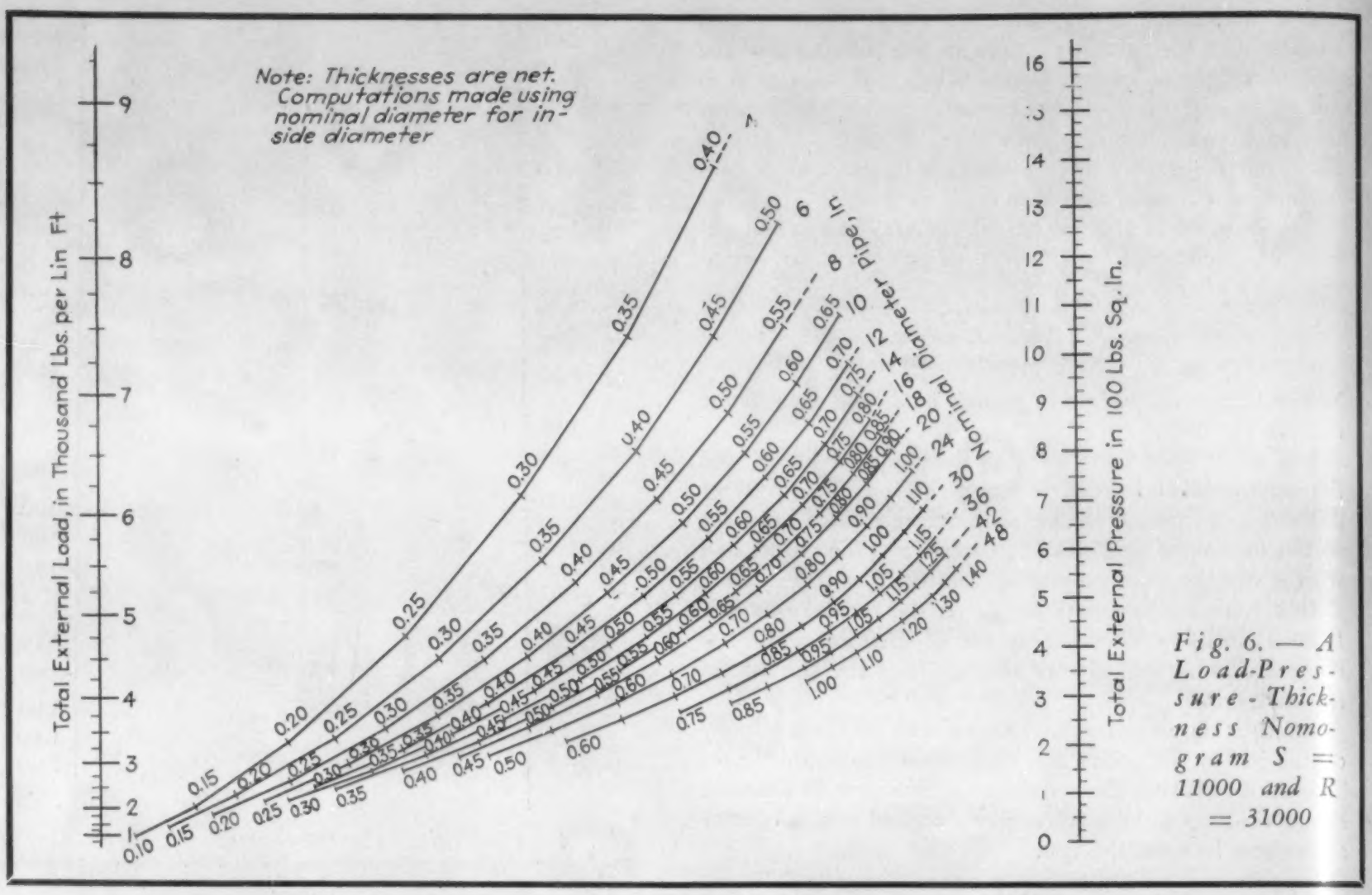

Note: Thicknesses are net. Computations made using nominal diameter for inside diameter
Total External Load, in Thousand Lbs. per Lin Ft
Nominal Diameter Pipe, in
Total External Pressure in 100 Lbs. Sq. In.

Fig. 6. — A Load-Pressure-Thickness Nomogram S = 11000 and R = 31000

greatest value of this type of nomogram may be realized by adapting it to some particular problem such as determining the amount of ferrosilicon to be added in the ladle to give a desired rise in silicon, or for determining the amount or percentage of steel to be added to decrease the silicon, etc. Nomograms constructed for the particular recurrent problems peculiar to each shop and for the particular ranges desired are always of greater practical value than the more generally applicable nomograms often published in the literature.[3]

To Figure Weight of Pipe and Thickness

Another nomogram found to be of value is shown in Fig. 5. This chart is used to find either the weight of pipe to give a certain thickness, or the thickness required to give a certain weight for a pipe of given diameter. The equation is:

$$\text{Wt. per Ft.} = 9.8t\,(\text{Dia.} - t)$$

The equation is linear in weight and diameter for any given thickness, so uniform outside scales were used for weight and diameter and the points on the scale for thickness were calculated and plotted.

The three examples given above illustrate the use of the nomogram for quick solution of relatively simple routine calculations, and this type of chart is of value in proportion to the frequency of its use.

Where Nomogram is a Necessity

There occur occasionally problems which are practically unsolvable except by some graphical method, and in these cases the nomogram is almost a necessity. From the equation developed by Schlick and Moore[4] for strength of cast iron pipe under combined tension and flexure there may be calculated the following equation relating trench load and internal pressure to the required thickness of cast iron pipe (see note):

$$\frac{2St}{D} - P = \frac{2St}{D}\left(\frac{.0795\,(D+t)W}{Rt^2}\right)$$

Where: W = External load — Lbs. per linear feet.
t = Required thickness of pipe—Inches
P = Total internal pressure—Lbs. per sq. in.
D = Inside diameter of pipe—Inches
R = Modulus of rupture—Lbs. per sq. in.
S = Tensile strength—Lbs. per sq. in.

For a given size and kind of pipe D, R, and S are constant, and when cleared the equation becomes:

$$(2R^2SD)t^4 - (R^2D)Pt^3 - (.01264S)W^2t^2 - (.02528SD)W^2t - (.01264SD^2)W^2 = 0$$

This equation becomes linear in W and P when the P scale is a uniform scale and the W scale a squared scale since P occurs only as the first power and W only as the second power.

Note: The relation developed empirically by Schlick and Moore[4] from studies of cast iron pipe for cast iron under tensile and flexural stresses is:

$$S - S_1 = S\left(\frac{R_1}{R}\right)^2$$

Where: S = Ultimate bursting strength
R = Ultimate crushing strength
S_1 & R_1 = Tensile and flexural stresses operating together.

In the cast of a pipe in service it is desired to substitute internal pressure for tensile stress and external load for flexural stress. When S is replaced by the value for bursting strength of a pipe $\left(\frac{2St}{D}\right)$ and R is replaced by the value for crushing load of a pipe $\left(\frac{Rt^2}{0.0795\,(D+t)}\right)$ the relation as given above is obtained

The t scale for a given size and kind of pipe may be plotted by determining the ultimate value of P necessary to cause failure when W = 0, and the ultimate value of W necessary to cause failure when P = 0 from the relatively simple formulae:

$$P\ (Ult) = \frac{2\,St}{D}$$

$$W\ (Ult) = \frac{Rt^2}{.0795\ (D+t)}$$

A nomogram so calculated is shown in Fig. 6. By connecting with a straight edge the total external load and the total internal pressure on the outer scales, the thickness of pipe which will just fail under these conditions may be read on the inner scales for each size pipe. This equation is extremely difficult to solve by any other than a graphical method, yet thousands of readings on the nomogram were made in recent work on specifications for cast iron pipe.

The examples of nomograms shown are those which have been used and found to be of practical value, and it is hoped that they may suggest similar applications for the use of other foundries.

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[1] Eldon K. Ralston, "How to Construct Nomograms for Use in Design", *Machine Design*, February, 1933, page 33.
[2] M. G. Van Voorhis, "How to Make Alignment Charts", *Product Engineering*, January, February, March, May, and July 1936.
[3] "Design Work Sheets—New Series". Compiled by *Product Engineering*. McGraw Hill Publishing Co., New York.
[4] "Strength and Elastic Properties of Cast Iron" by W. J. Schlick and Bernard A. Moore. *Bulletin No. 127* of Iowa Engineering Experiment Station, Iowa State College. Page 29.

Editorial

(Continued from page A 43)

started, there were exported over 2,798,800 tons. Thus the total scrap exports for the 10 years have been 8,779,350 tons—a yearly average of over 877,930 tons. The extent of the expansion in foreign demand in the last three years is measured by the fact that the 1934 to 1936 total of over 5,980,500 tons is 68.1 per cent of the 10-year total. Thus far in 1937 the movement continues but on a somewhat diminished scale from the 1,993,500 tons yearly or over 166,000 tons monthly of the 1934-1936 period.

In the steel making as well as in the cast iron industry the metallurgical use of scrap in the charge has expanded rapidly in the last few years. To no little extent has it displaced pig iron. Because of the growing production of electric steel, where no pig iron is necessary, demand for scrap has increased. Thus the very large foreign demand for scrap is a menace to our domestic operations.

Two thoughts are suggested by these facts. One is that the larger use of scrap in iron and steel making is a testimonial to the constant improvement in metallurgical operations and a refutation of the old theory that a substantial proportion of virgin metal is necessary to produce a high-grade material. The other is that, with the growing use of alloying elements and their greater accumulation in even plain steels, the export of such elements is, or at least may be, no small item particularly in the case of those which are not lost by remelting. Figures as to the extent that alloy steels enter into these exports would be both valuable and interesting.

In view of the situation now prevalent, approaching a menace to domestic iron and steel operations, is not some thought by the Administration necessary and advisable as to a possible embargo or rationing of scrap exports?—E. F. C.

Steel for Bicycles

One of the interesting revivals in the sporting world, which is having a pronounced effect on the increased demand for steel, is bicycling. During 1936 there was a distinct tendency to a greater use of the bicycle—a vehicle of transportation which over 40 years ago, or in the "gay nineties," was then as popular as the automobile is today.

According to estimates of the American Iron and Steel Institute, this larger use of the bicycle resulted in orders for 15,000 tons of steel from American mills—by far the largest amount ever bought in one year by makers of bicycles. Last year more than 1,200,000 bicycles were manufactured, regarded as probably an all-time record for one year. It is twice the 1935 output and nearly four times the average number made between 1928 and 1934. The previous record bicycle year was 1,182,700 in 1899.

An interesting fact is that the bicycle of that early period was far less sturdy than the one of today and hence took less steel. It is consequently heavier today than in the early period. This is contrary to the tendency of today when lightness in weight with no sacrifice in strength is the rule—particularly in the transportation industry. Witness the expanding use of the low-alloy, high elastic steels. In the "bike" of 40 to 50 years ago, only 12½ pounds of steel was incorporated but in the 1936 models about 25 pounds is said to go, mostly as tubing and strip steel in the rugged frames and streamlined mudguards, head lamps and horns. Other metals than steel of course are consumed.

Is there not an opportunity here for the application of heat-treated alloy steels so as to lighten, at no great extra cost, the weight and offer the bicyclers less burden to propel? It would seem that the present-day bicycle should not weigh twice that of the "gay nineties."—E. F. C.

Alm - Aluminum!

In order to purge the German language of all "alien" terms, the National Socialist Government of Germany has gone to extremes little believed possible only a few years ago. Thousands of alien words are being dropped by official edict to make room for genuine German words, says a dispatch to the *New York Times* from Berlin.

One of the most glaring of these changes involves the metal aluminum. Henceforward this will bear the designation "Alm"—though for a time it will appear as "alm (aluminum)." Later the parenthetical word will be dropped! "Automobile" will give way to "Kraftwagon" and "export" and "import" will be banished totally for "Ausfuhr" and "Einfuhr." The name of Einstein's theory of relativity is to be tossed out of the German language. The term employed up to the present has been "Relativitaetstheorie," now considered of foreign origin. In its place (and taking up more space!) there has been ordained—*Bezueglichkeitsanshauungsgesetz!* How fortunate that a 31-letter word was not adopted for aluminum. —E.F.C.

Courtesy: Bethlehem Steel Co.

Charging Molten Pig Iron into the Open-Hearth Furnace

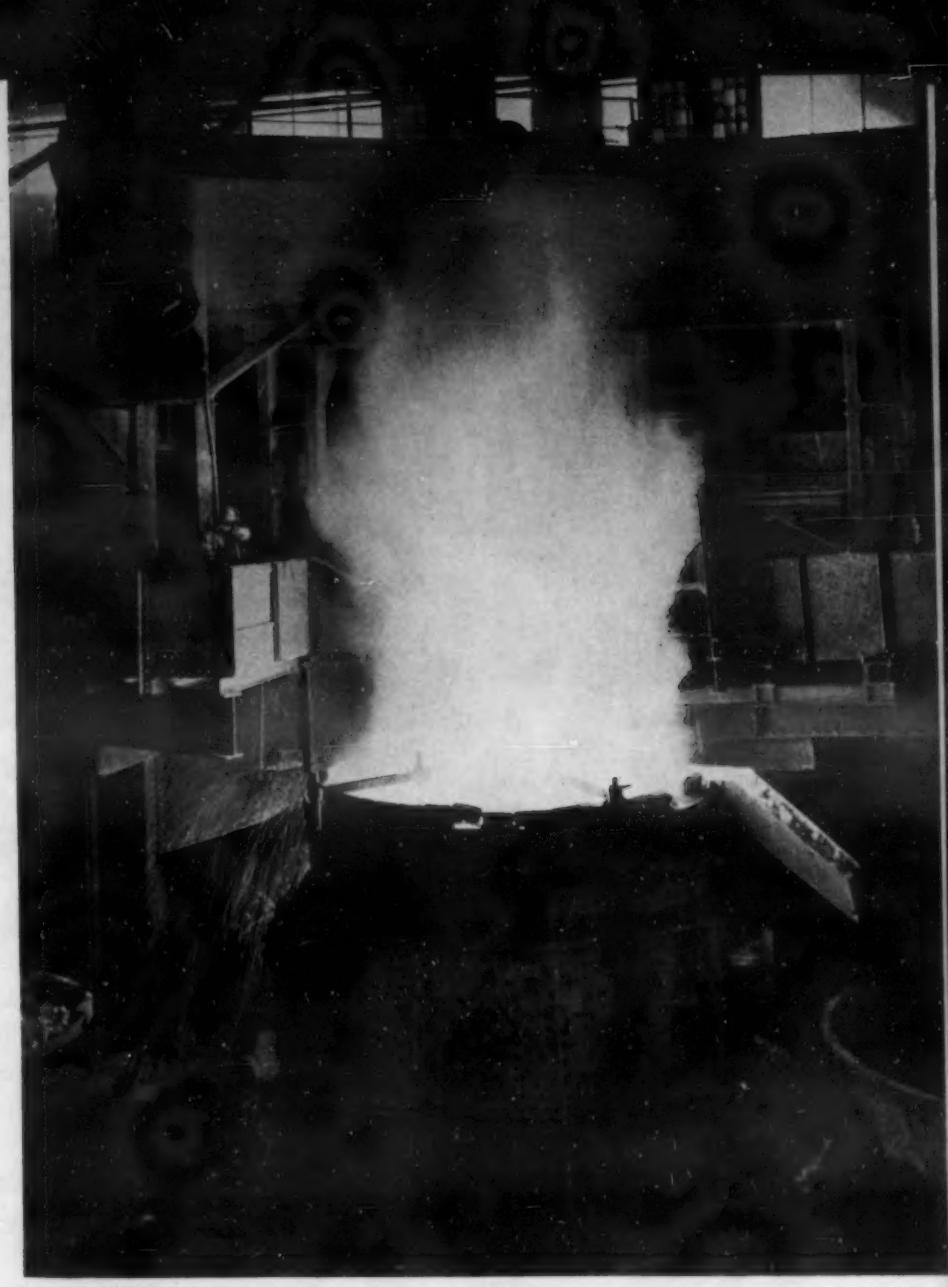
Residual Metals

IN OPEN-HEARTH STEEL

by John D. Sullivan

and R. A. Witschey

Battelle Memorial Institute, Columbus, Ohio



Tapping a Large Open-Hearth Heat. (Courtesy: Climax Molybdenum Co.)

THIS IS THE SIXTH of an annual series of articles on residual metals in open-hearth steel. Previous articles[1] discussed the source of residual metals, and their significance in steel. During the past year the technical and economic significance of scrap was discussed by Williams[2].

Data from 21 Companies

The results reported in this article for the year 1936 are from 21 steel companies in the United States and Canada representing an annual tonnage capacity of approximately 8,450,000 tons. Samples are taken from representative heats before alloy additions are made, and in general indicate the composition of the plain carbon steel base used in the various plants before adjustment of the composition by alloy elements. At the end of the month composite samples are made and sent to Battelle Memorial Institute. Here, annual composite samples are made for analysis. The study continues from year to year, and this report brings the results up to date.

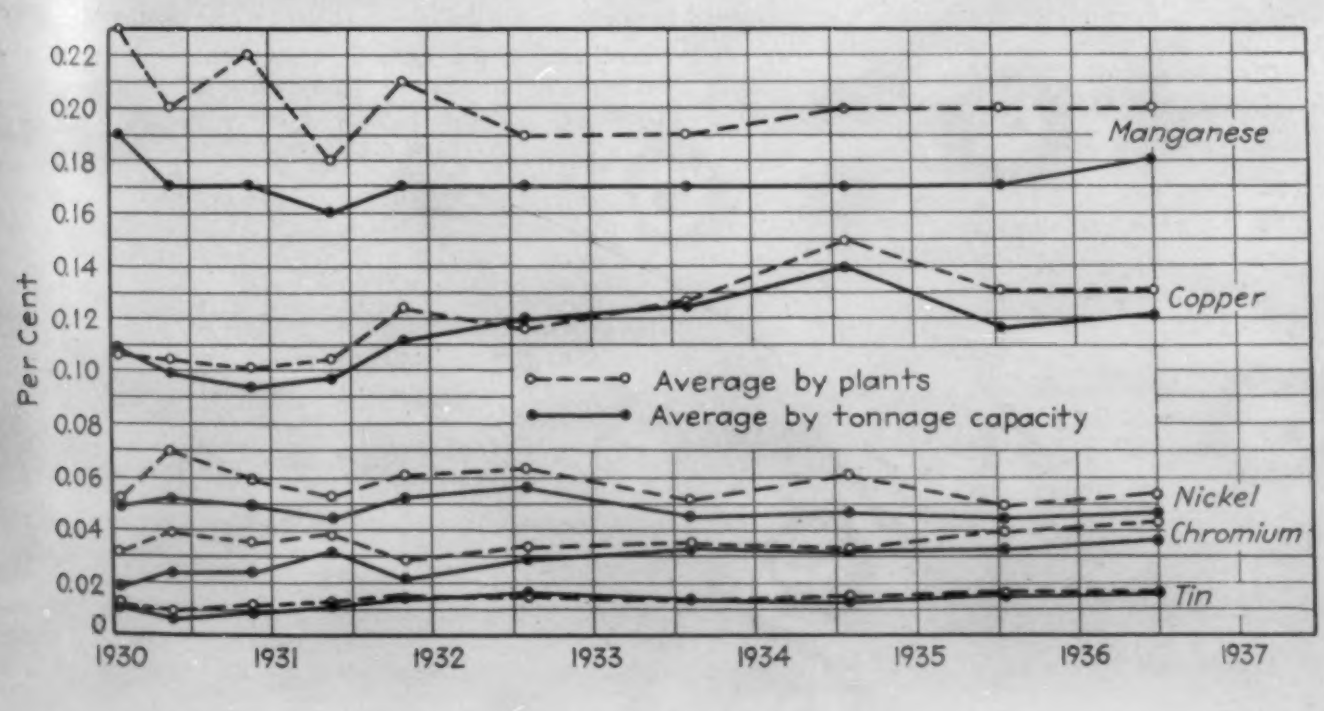


Fig. 1—Average of All Plants

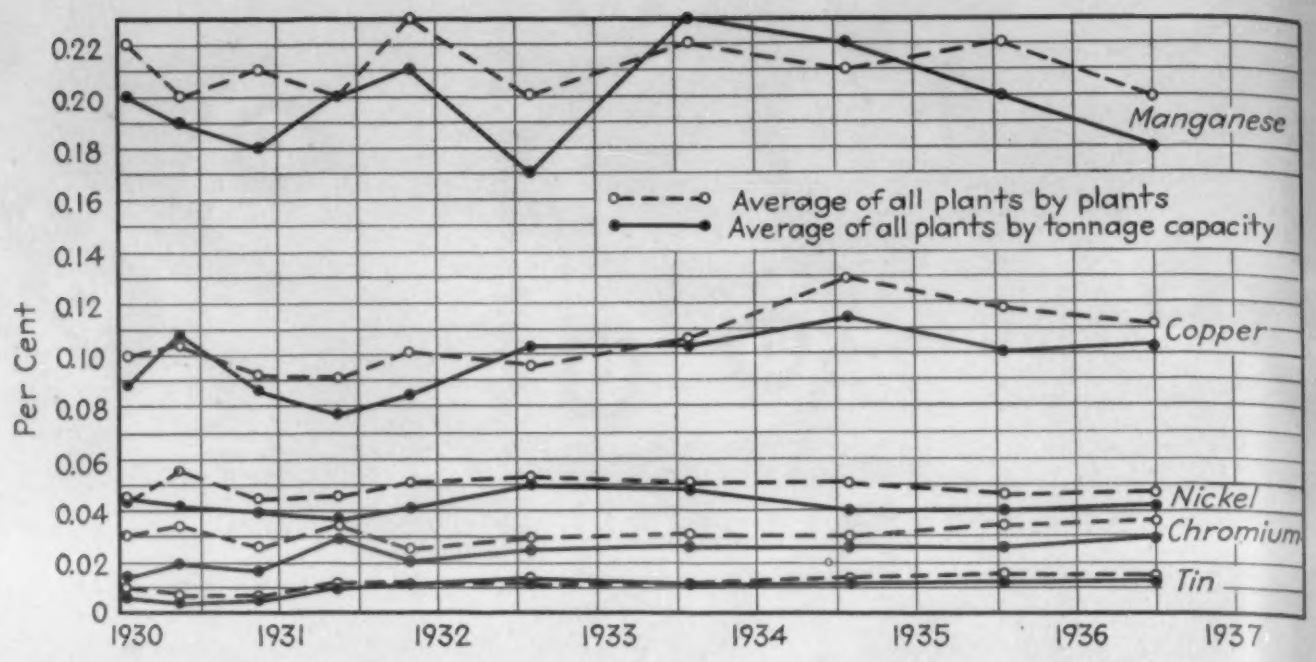


Fig. 2—Average of 10 Plants that Have Cooperated in All Periods. Tonnage Capacity—3,700,000 tons.

Methods of analysis for tin, nickel, copper, and chromium were given in the 1935 paper, and for arsenic and antimony in the 1936 one. For the current period analyses were made for tin, nickel, copper, chromium, and manganese. The data are given in Figs. 1 and 2. The average of all plants for any period refers to those plants that cooperated in that period. The year is plotted as the middle of the interval represented. The 10 plants that have cooperated in all 10 periods represent an annual tonnage capacity of approximately 3,700,000 tons.

No Marked Changes in 1936

In comparing average values of residual metals for the current period with the previous year it will be seen that there have been no marked changes in the amount of any residual metal except manganese which is not a true residual metal because it is intentionally added in the pig iron so as to finish a heat with a predetermined manganese content.

In previous papers curves were given to show the relationship between the scrap ratio in the charge and (a) total steel production, and (b) prices of pig iron and scrap. Statistical data are not complete for 1936 so the curves are not given this year. The percentage of scrap in scrap plus pig iron was calculated to be 59 in 1935. The percentage is estimated as being about 57 per cent for 1936, although final statistics may show that this value is somewhat in error. During the past year the United States Bureau of Mines issued the first of an annual series of statistical reports on ferrous scrap and pig iron used in the United States[3]. This report on a total coverage of 99 per cent of the open-hearth furnaces in the United States gave the percentage of scrap used in 1935 as 58 per cent, which is in excellent agreement with our calculated value of 59 per cent.

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[1] Clyde E. Williams and John D. Sullivan. "Residual Metals in Open-Hearth Steel." METALS AND ALLOYS, Vol. 3, 1932, page 240.
Clyde E. Williams and John D. Sullivan. "Residual Metals in Open-Hearth Steel." METALS AND ALLOYS, Vol. 4, 1933, page 151.
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John D. Sullivan and Ray A. Witschey. "Residual Metals in Open-Hearth Steel, Arsenic, Antimony and Others." METALS AND ALLOYS, Vol. 7, 1936, page 171.
[2] Clyde E. Williams. "The New Technical and Economic Importance of Iron and Steel Scrap." Yearbook of the American Iron and Steel Institute, Vol. 26, 1936, page 185.
[3] Richard J. Lund and H. W. Davis. "Consumption of Ferrous Scrap and Pig Iron in the United States in 1935." Report of Investigations 3329, Department of the Interior, Bureau of Mines, 1936, 16 pages.

Erratum

On page 74 of the March issue at the end of the second column there is a table of "Calculated Planes of Diffraction Rings." There is an error in the fourth column of the table, due to faulty proof reading after corrections had been ordered. This column should read as follows:

Indices
$110_{(2)}$
311
$111_{(2)}$
$200_{(2)}$
331
$210_{(2)}$

The article was entitled "An X-Ray Study of Preferred Orientation in Rolled Copper," by H. V. Anderson and G. L. Kehl, of Lehigh University, Bethlehem, Pa.

A Poetic Protest!

The Joint Committee of the A.S.T.M. and the A.S.M.E. on the Effect of Temperatures on the Properties of Metals held an executive session during the Group Committee Meetings of the A.S.T.M. in Chicago early in March. The fact that non-members could not attend gave rise to the following poetic protest on the "lock-out":

Dedicated to the Joint Committee on the Effect of High Temperature on the Physical and Ethical Properties of Metals.

The power plant man begins to weep
When his flange bolts begin to creep.
He has a talk with Brother Clark,
But still his mind is partly dark.
He then seeks French in his sad pickle,
And French, he says, "Put in more nickel"
Then he to Kanter straight doth go,
Who states "Planck's constant is too low"
Then to Battelle he takes his quest,
They say, "Don't trust the short-time test."
The power plant man goes home again,
Then to an asylum for th' insane.—H.F.M.

(This report from an unofficial sub-sub-committee dealing with "Project No. X13" on Poetry?, was read at a recent meeting of the A.S.T.M.-A.S.M.E. Joint High Temperature Committee but will not appear in the official reports of those bodies, the sub-sub-committee on Publicity!, "Project No. M1," having granted exclusive rights of publication to METALS AND ALLOYS.)—H.W.G.

Testing Metals for Severe Service

AN EXTENDED ABSTRACT

by H. W. Gillett

IN THE PAST MONTH attention has been directed to some of the activities of the American Society for Testing Materials which relate to the evaluation of metals in severe service but in which services the life of present materials, though long, is not yet long enough to satisfy the engineer.

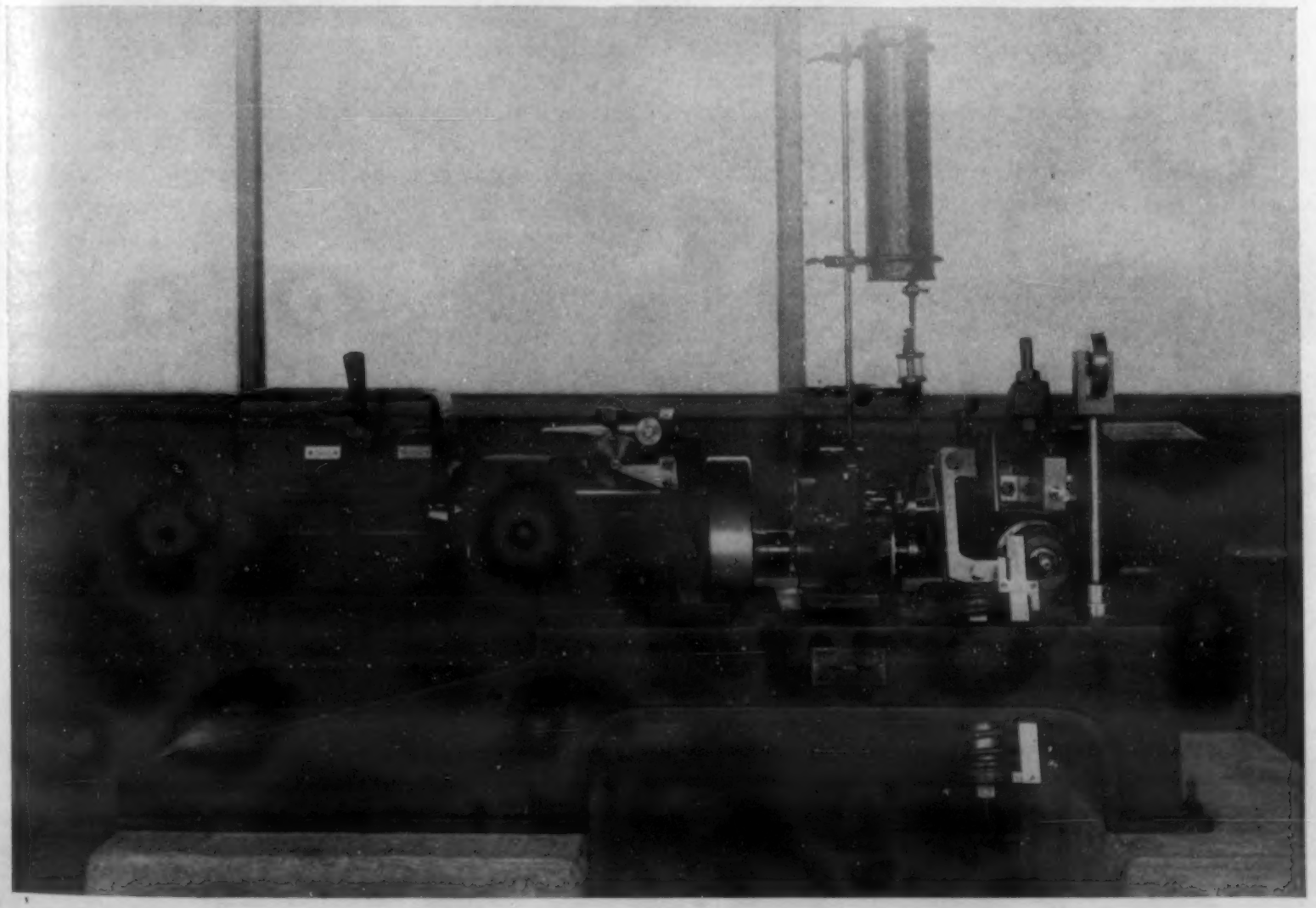
At the "Committee Week" meetings in Chicago one crowded evening was devoted to papers on Corrosion Testing. The all-day Lubrication Symposium, while aimed primarily at lubrication and motor fuels, dealt with bearing life and its evaluation. Committees and subcommittees struggled with problems on fatigue of metals, properties of metals at high temperature, behavior of special corrosion and heat-resisting alloys, and life of electrical resistors in controlled-atmosphere furnaces. At the regional meeting in Philadelphia early this month there was a Symposium on "Wear of Metals."

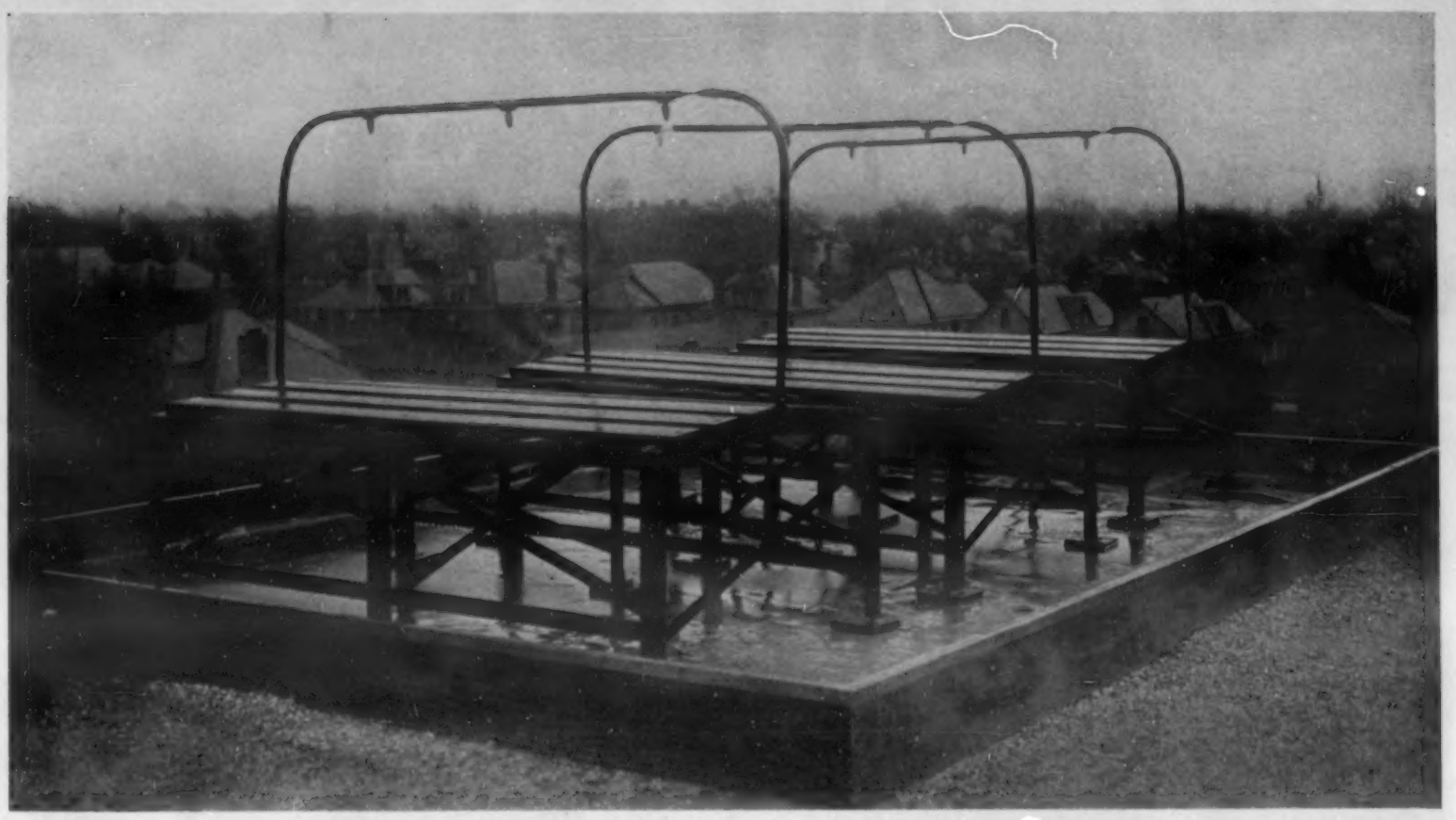
Problems and Methods of Attack, Similar

The general pattern of the problems faced and of the ways in which they have to be attacked is strikingly similar. Moreover, the conclusions of those who have spent years in the study of methods of evaluation of resistance to the various modes of deterioration in regard to the feasibility and advisability of standardizing the methods of testing are remarkably alike.

Controlled corrosion testing, as a cooperative matter through committee action, has the longest history, the A.S.T.M. exposure work which established the value of copper-bearing steels in atmospheric corrosion, having passed its twentieth year. Fatigue testing, not much younger, has reached a definite goal in that the endurance limit can be definitely evaluated and reported in terms of pounds per square inch at a definite number of cycles. Yet, as

An Amsler Testing Machine Rigged for Lubricated Wear Tests. (Courtesy: Battelle Memorial Institute)





A Corrosion Testing Rack with Provision for Intermittent Spray. (Courtesy: Battelle Memorial Institute)

Prof. H. F. Moore remarked at the Fatigue Research Committee meeting, the more he found out about fatigue, the more points he found upon which he knew nothing. Questions of axial vs. rotary loading, speed of testing and size of specimen remain somewhat obscure. Nevertheless different laboratories can take the same material and, by applying the knowledge gained from the combined experience of the experimenters as to the effect of fillets and surface finish, they can secure consistent results even though the specimens and testing machines have not been officially "standardized."

The Joint High Temperature Committee has worked out codes of recommended practice for short and long-time tensile testing at high temperatures and, while some details remain to be worked out, it has shown, by preparation of a very uniform steel and cooperative study of it in several laboratories, that when proper precautions are taken the different laboratories come out with reasonably agreeing results. Thus the way is opened for the study, by anyone who wishes to, of those variables which govern the load-carrying ability of metals at high temperatures, and the reporting of results in such terms that they can be understood, accepted, and comparisons made.

In this there is no attempt to fix every detail of specimen or testing method which may properly vary with the particular problem in hand, but there is an earnest attempt to seek out the important variables and make it imperative that they be controlled.

Several Objects Involved

In all this severe service work, the object may be one of several. It may be desired to develop a better alloy and to indicate by laboratory tests whether it is really better without having to wait for long-drawn out service tests. Or, in order to make an economic choice between competing materials, it may be necessary to estimate in terms of years what their life will be. Again, the desire may be to apply an acceptance test to insure that the ability of a given lot to stand up in service is equal to that of previously used material.

The two latter, involving exact quantitative evaluation, are extremely difficult in these fields because of the slow rate of attack and the danger of altering the conditions of attack when an attempt is made to accelerate it. The first, in which definite, even though only qualitative, information will serve, is ordinarily more feasible to accomplish. But in general the three different aims are almost always present together.

Principles of Corrosion Testing

The paper by Borgmann and Mears delivered at the Symposium on Corrosion Testing in Chicago, on "Principles of Corrosion Testing" could very well be generalized, for the same general principles apply well to the whole problem of severe service testing. Taking these principles, together with the more detailed comments on specific types of testing as discussed by Rawdon, by McKay and LaQue and the other authors at the corrosion symposium, one may say that these different experts are in substantial agreement that, first and foremost, one needs an accurate picture of the mechanism of deterioration and that, until this has been attained, standardization is worse than useless, since the first stab is likely to leave out some of the variables that count and, if different observers try to get consistent results so their data may be inter-compared, there is lack of consistency and comparability.

Hence, too early standardization of methods is futile. When all pertinent details have been rounded up and proper control incorporated in the method, then different observers will get agreeing results, and even though the test so worked out should bear less actual relation to service than its proponents first thought, the test will serve as a means of tying in together the results of different investigators, so that the "standardization" of such tests has some value.

Correlation with Service

Correlation of long-time service results with those of such tests will show whether they have much applicability or not. It often turns out that a specific test has value only in relation to a given type of service or to a given class of

alloys. Borgmann and Mears warn against accelerated simulated service tests because of the danger of altering the mechanism of attack, but speak respectfully of "Special Property Tests," i.e., tests which were usually originally promulgated as an accelerated test but which turn out to indicate only some one particular factor that has an important bearing on corrosion. With a sufficient background of correlation with service, these tests can serve as acceptance tests, not that they truly evaluate corrosion-resistance, but they increase the chance that the material tested, being similar in composition and structure to a material that has done well in service, and being similar also in relation to the "special property," may also act like it in service. Copper sulphate tests to evaluate the film-forming properties of chromium alloys, corrosion-fatigue tests, salt-spray tests and the like are cited as examples.

These authors, as do the authors of the other papers and discussions at the Corrosion Symposium, list the variables concerned, urge control of these variables in the tests and detailed reporting on this control so the reader may draw his own conclusions and stress the specific effect of variations in the corroding medium. That is, corrosion is a dual matter between the corrodent and the metal corroded, not a specific property of the metal. Avoidance of rigid specifications in testing that would throttle originality, but some standardization of methods and of expression of results for the sake of intercomparisons are stressed by all.

Symposium on Wear Testing

The factors involved in corrosion testing that were brought out at the symposium will be brought out in a correlated abstract on recent advances in the knowledge of corrosion which is now in preparation by an expert on the subject. So we will turn to a résumé of wear testing, leaving the symposium papers on wear problems in different types of service to be summarized later.

In the discussion of wear testing methods at the wear symposium, very much the same line of thought was advanced as at the corrosion symposium. Wear, like corrosion, is a mutual matter, and depends on conditions of service; it is not at all an inherent specific property of a metal apart from its environment.

Types of Wear

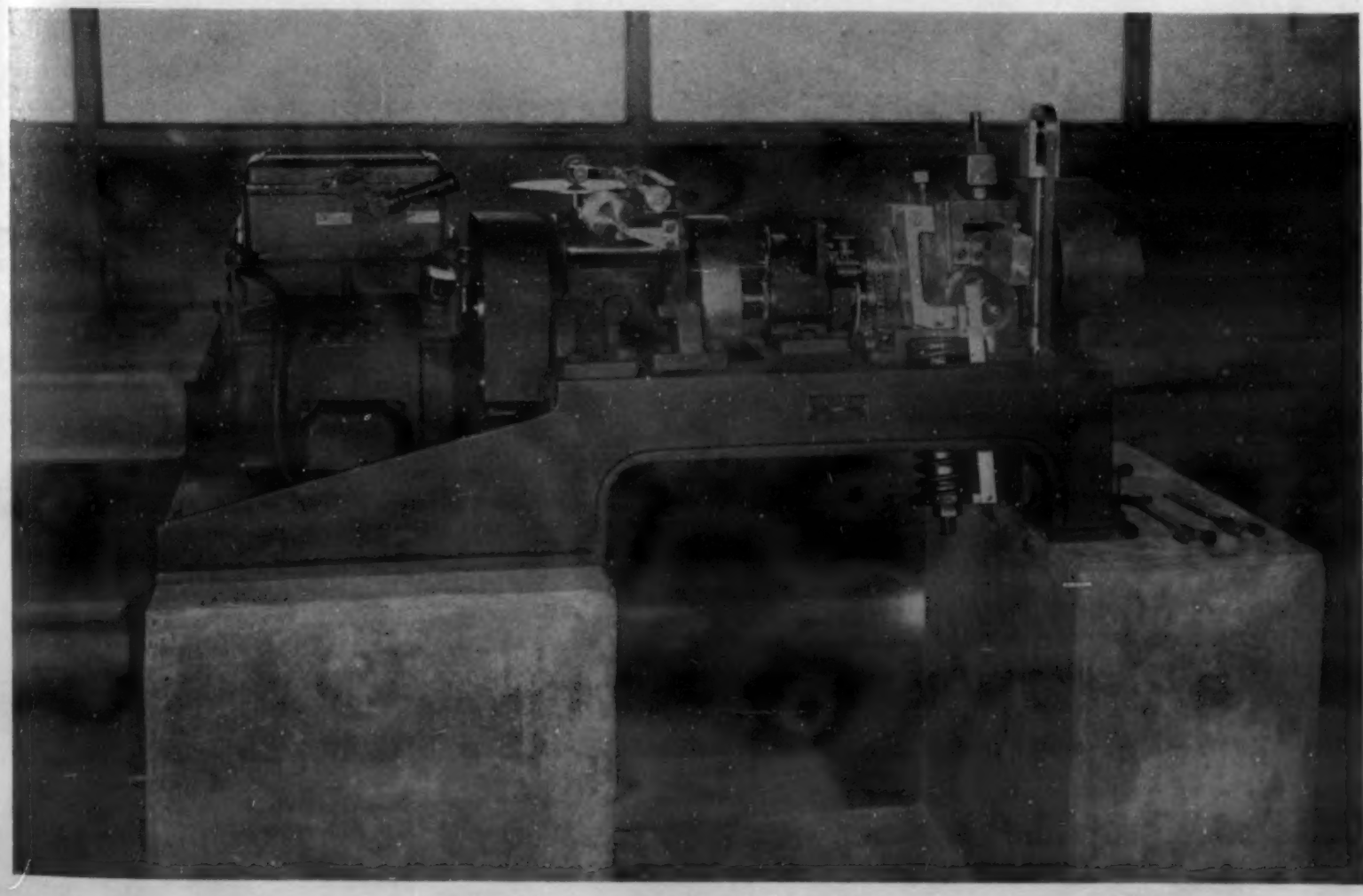
Wear is the undesired gradual change in dimensions in service under frictional pressure. Non-metals pressing against a metal produce wear such as that on tools for tilling the soil, jaw crushers, sand pumps and the like. The metal's resistance to this type of wear depends on surface hardness, to resist penetration of the cutting particle, and, if penetration occurs, resistance then depends on toughness to resist being torn off. Some optimum combination of hardness, toughness, and microstructure (grain size and presence or absence of brittle constituents at grain boundaries) is then called for, and each factor may be studied by "Special Property" tests. In simulated service tests the abradent must represent that occurring in service. Sand blasting tests and the tests in which a specimen is dragged around in a mass of dry or wet sand may place a series of specimens in one order or in a reverse order, according to the abrasive used, so that great care has to be taken to make the test one of the metal rather than of the abrasive.

Another type of abrasive wear occurs when dirty oil passes through a bearing when, if the bearing lacks "embedability," the grit may be forced into contact and score, one or both, the shaft and bearing while, if the bearing has the properties of a lap, it may partly engulf the grit and its own oil film may not be seriously broken through.

Non-metals may wear metals, a silk casting line will ultimately cut a groove in hardened steel guides, and fiber, plastics and hard rubber wear cutting tools amazingly. Little is known about this type of wear.

Metal-to-metal wear occurs under sliding friction, as in bearings, gears, brakes, rails and wheels, etc. When the mating parts are lubricated, the ability to hold an oil film

Amsler Machine for Wear Testing of Metals. (Courtesy: Battelle Memorial Institute)

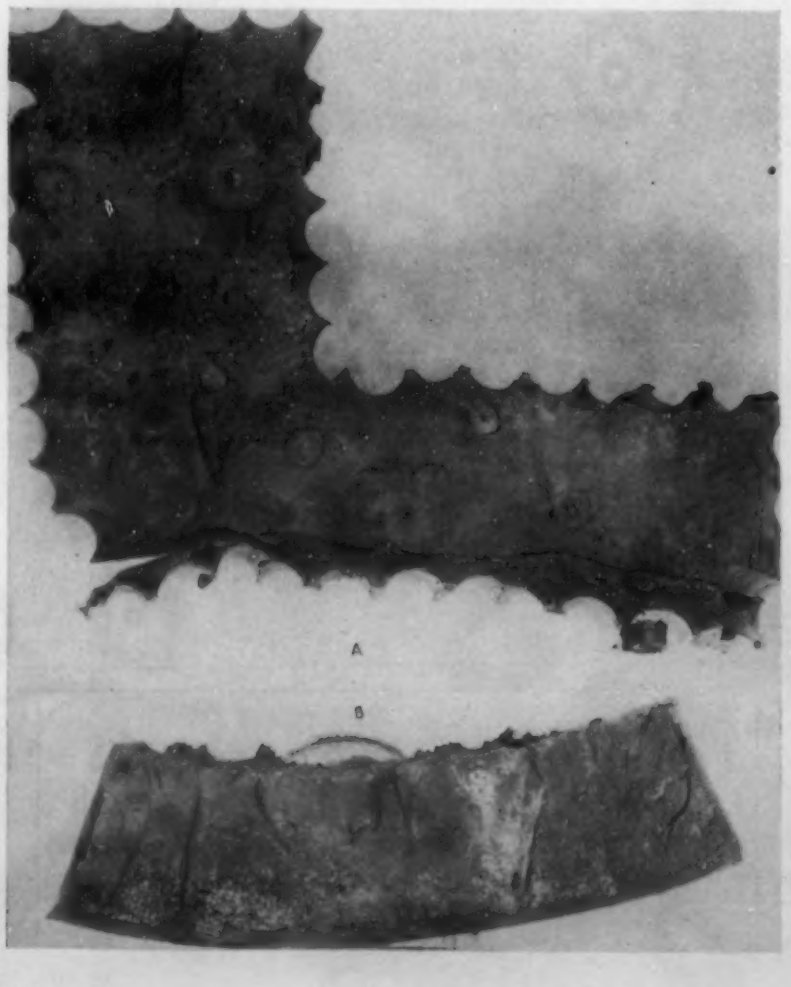


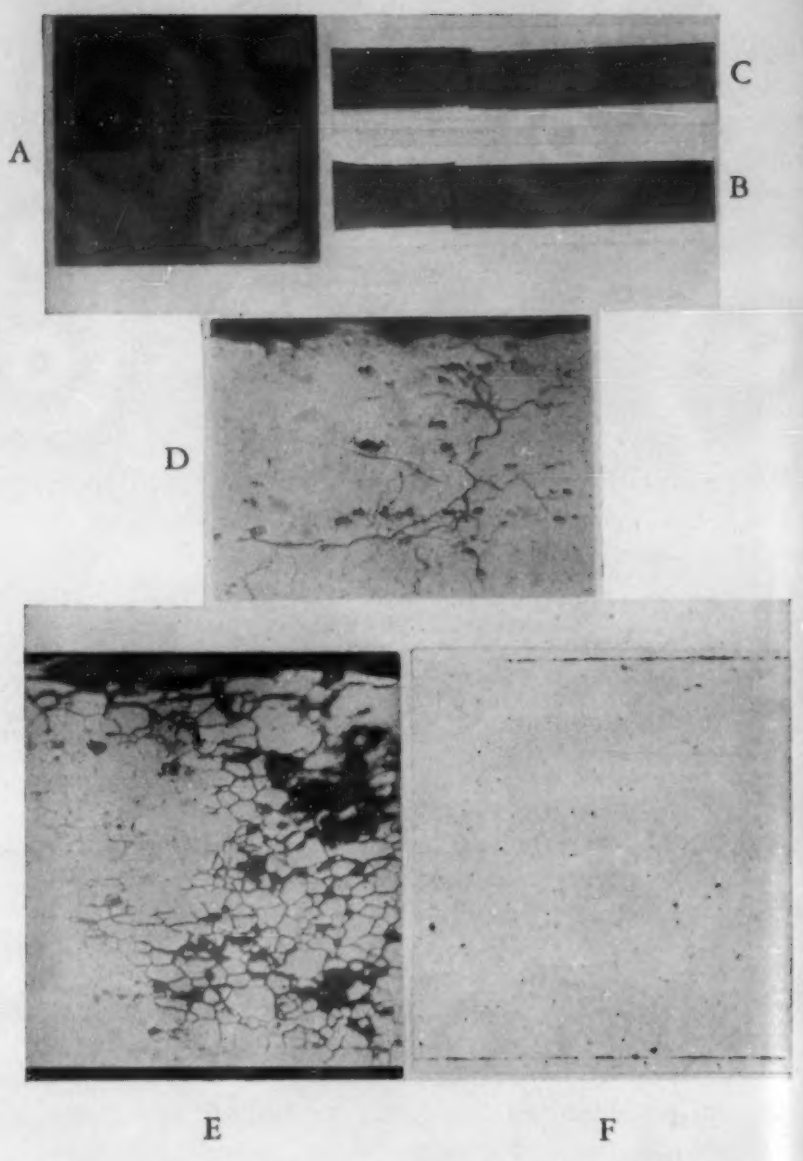
against bearing pressure in stopping and starting is of importance. Specific property tests for "oiliness" of lubricants have been suggested and, if they worked, they could be reversed to test the oil-holding power of the metal, but none of them seem of much value. When the oil film has broken down or when no lubricant is present, failure occurs in two principal ways (a) by work hardening and embrittlement of the surface, followed by spalling, (b) by incipient welding or seizure, the mating metals being pressed into true metallic contact, welding together locally, then being torn apart.

Weldability and Work Hardening

Work hardening can be studied, as a "specific property" test. Weldability, which naturally depends largely on temperature and pressure, to produce closeness of contact, and propensity toward formation of a non-metallic film that presents metallic contact and thus avoids welding, may be studied by specific tests designed for the purpose, like those described by Mochel[1] and by Bolton[2] and in the Amsler wear-testing machine. A notable case of film-formation is in hypoid gears which, when made of the usual materials, will show no life at all unless some special lubri-

Vibration and Corrosion. It is well known that continued vibration of a metal structure may lead to disastrous results. If the metal is corroded at the same time, the probability that failure will occur is enormously increased. A shows a portion cut from the head of a cast steel piston of a Diesel engine. The cracks showed the characteristic features, B, produced by fatigue stressing of the metal. Subsequent investigation revealed that the oil used as a cooling medium on the inside of the piston had become contaminated and that severe corrosion was accompanying the vibratory stressing of the piston. The cracks originated on this side of the piston. (Courtesy: H. S. Rawdon, Bureau of Standards.)





Embrittlement of Light-Alloy Sheet by Weathering. Some metallic materials, especially if in the form of sheet, may become brittle when exposed continuously to the weather though the general appearance may not be greatly altered. Structural examination shows that corrosion of a peculiar type has occurred. In A, the degree of embrittlement which may occur in such a material has been demonstrated by bending the sheet. This can be shown more precisely by a tensile test as in B. A companion material immune to corrosion of this kind is shown in C. The corrosive attack is intergranular in nature, the bond between adjacent grains being weakened by the attack as shown in D, typical of material B after weathering. The same effect can be produced by laboratory corrosion tests. E, which is a complete section through a sheet, shows the weakening effect on the structure produced by 6 mos. continuous exposure to NaCl spray. F shows a companion material which completely resisted such a corrosive attack for 9 mos. Such a material can be depended upon in service to retain its initial strength and toughness. (Courtesy: H. S. Rawdon, Bureau of Standards.)

cant is present that will combine chemically with the gear to produce a non-metallic film. This film is actually a structural part of the gear in operation.

The fit and finish of mating parts enter into wear. If tiny promontories on one engage with like promontories on another, something has to give way. This case is somewhat analogous to that of non-metallic abrasives in that hardness plus toughness tend to resist it. The disposal of

metal debris, torn off in this fashion, is a factor in further wear. If it is washed out of contact the result will be milder wear than if it is held between the mating parts. Thus there may be a difference between rotating and reciprocating wear.

Corrosion and Wear

Corrosion and removal of the products of corrosion enter into some types of wear, and automotive cylinder wear is considered to have a good deal of that sort of component.

The ring and cylinder case brings up another important point—metal-to-metal wear involves the degree of wear on each of the mating parts. One might rig up a test outfit, evaluate a series of piston ring alloys against one cylinder alloy, and select the ring alloy that behaves the best, only to find that in service against a different cylinder alloy it may, though itself being wear-resistant, nevertheless wear the cylinder far too rapidly. Test methods should then enable measurement of wear on both the worn and the wearing part, and tests should cover the whole range of materials against which the one being studied will have to work.

Just as in the case of "accelerated corrosion tests," the tests become misleading if the rate of attack is so accentuated that the mode of attack is altered. Hence one criterion of a reliable wear test is that it shall produce worn specimens that, in every stage of wear, look like those at a comparable stage in wear in service. Acceleration must therefore be approached cautiously and no wear test adopted that does not invariably place in the proper order materials known to act well and badly in service. This means that the soundest test for wear is full-size equipment, or a scale model, set up in the laboratory where the conditions of service can be controlled, recorded and duplicated. Such tests are costly and patience-trying in cases where the rate of wear is low, but they give reliable results.

There is a natural tendency, when a wear problem arises, to think that any method of slowly removing metal will evaluate the wear resistance; so holding it against a grinding wheel, rubbing it on abrasive paper or some analogous method is tried. Scores of such tests have been devised and tried, with uniformly poor results because the mode of attack was not analogous to that of service. Cutting a gouge in a specimen by a rapidly rotating toothless saw, as in the Spindel machine that has been much tried abroad in the attempt to throw light on wear of rails and wheels, falls into this category. Such tests are "special property" tests, not wear tests, and seldom give more information than a mere hardness test.

Standardizing Wear Tests

Very little attempt has been made to standardize wear testing, few observers use more than one wear test apparatus, and swapping specimens among observers is practically unheard of, so intercomparability is lacking. The procedure in the Amsler test has been thoroughly described by many writers and the machine is available on the market so that it comes the nearest to a standard test for purposes of comparison. So rarely does it closely approximate the conditions of service, save perhaps as to rail and wheel wear which it was designed to study, that most wear problems require that a special machine be built to more closely

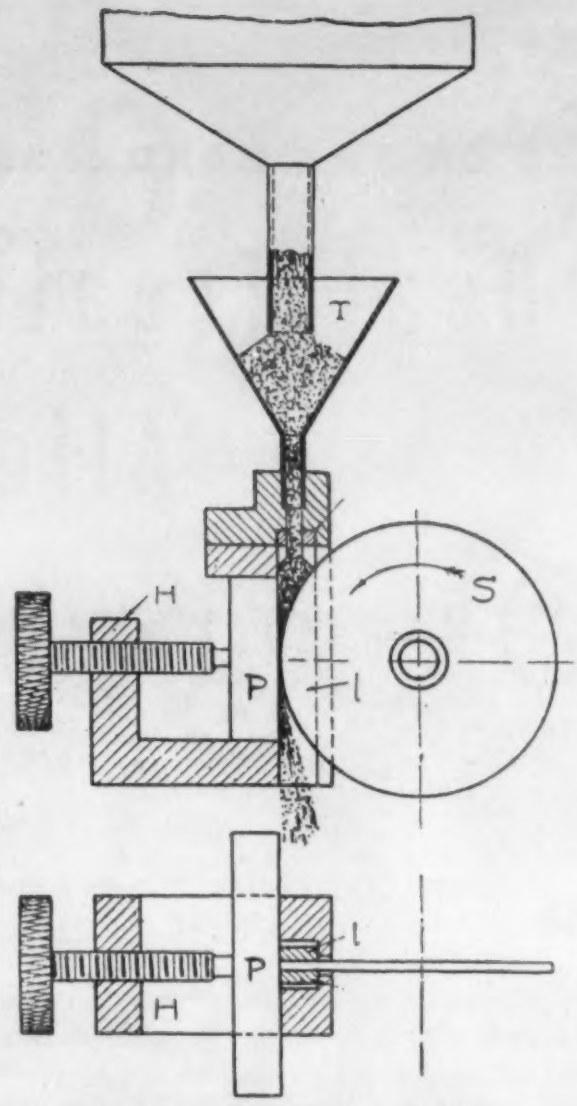


Diagram Showing Brinell's Method for Investigating the Resistance to Wear of Materials in Frictional Contact with Sand. (Courtesy: Herman A. Holz, New York)

approximate the conditions of the service in question. This appears to be the path of progress. Certainly wear is not an inherent property, and no "universal wear-test" can be devised, any more than can a single universal corrosion test be devised without regard to the conditions of service.

Indeed, wear testing is fortunate in that no pseudo-test has been advanced which producers had to use no matter whether it has any relation to service, in the way the salt-spray test has sometimes been forced on producers of metals to resist corrosion in applications outside of marine or seashore service. An intelligent mode of attack is that employed by Parker[3] who studied wear of tire chains by field tests with a fleet of cars, and analyzed failures into a combination of impact and abrasion by non-metallics. He then set up impact limitations and subjected materials falling within those limits to abrasion on a grinding wheel, varying his test conditions till the grinding wheel placed specimens in the same order as did controlled service tests.

The exposure, or "simulated service," tests of the A.S.T.M. corrosion committees have given far more real information than have laboratory tests. In the province of wear testing, and other "severe service" testing, it would be well to study the corrosion analogy and adopt a philosophy of testing that will duplicate the successes and avoid the failures that have occurred in the more deeply tilled field of corrosion.

References

[1] N. L. Mochel. *Proceedings*, A.S.T.M., Vol. 28, Part II, 1928, page 269.
[2] J. W. Bolton. *Mechanical Engineering*, Vol. 58, 1936, page 165.
[3] Parker. *Proceedings*, A.S.T.M., Vol. 28, Part II, page 332.

NOTES ON THE HARDNESS AND CONDUCTIVITY OF

Heat-Treated Copper Castings Alloyed with Zr and Be

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THE ALLOYS OF COPPER and zirconium have been described by Allibone and Sykes (*Journal,* Institute of Metals, 1928, No. 1, page 173, and 1929, No. 1, page 179) and according to these investigators zirconium hardened copper without remaining in solid solution to any appreciable extent. This characteristic led to the thought that copper castings might be hardened by zirconium without decrease in conductivity such as is produced by most other hardening agents.

To investigate this question some alloys were made up and tested, using "TAM Cupro Zirconium" of high purity as the source of zirconium. It was found at once that the alloys were susceptible to temper-hardening, and the work was therefore planned along the same lines as the previous research on the temper-hardening copper-titanium alloys, reported by one of the authors in METALS AND ALLOYS, October, 1936.

Pure copper was melted in Dixon clay-bonded graphite crucibles in a gas-fired furnace, using a glass cover on the melt and about 0.03 per cent of calcium, magnesium and silicon for deoxidation. The zirconium was added at a temperature of about 2325 deg. F. in the form of the Cu-Zr alloy mentioned above, containing about 15 per cent zirconium and less than 0.2 per cent of silicon, iron, titanium, or aluminum. The glass was removed before adding this alloy, which dissolved readily, and gave 76 to 88 per cent recovery of zirconium. The casting properties of the alloys containing zirconium were better than with titanium, the tough skin being less in evidence on the melt so that the castings came cleaner.

The test specimens were cast in the same way as was described in the previous paper on titanium alloys, and to the same pattern. The heat treatments and tests were also conducted in the same manner.

Copper-Zirconium Alloys

The first series of alloys was made with zirconium contents of 1.45, 2.4, and 3.24 per cent, respectively. Two bars were made of each alloy, and one was held 2 hrs. at 1650 deg. F. and quenched in water. A number of specimens were cut from each and the following heat treatment program was carried out to determine the maximum hardness obtainable by tempering: Heating at 500, 750, 850, 950, 1050 and 1200 deg. F. for 1, 8, 16, 24 and 48 hrs. respectively at each temperature. The results of hardness tests on these samples are plotted in Fig. 1.

At each temperature, the maximum hardness was obtained from the quenched bar, tempered at 750 deg. F., but it was necessary to continue the treatment for 48 hrs. in order to develop this. Further tempering at this temperature was then tried and the hardness curve definitely levelled off after 144 hrs.

The maximum hardness after 24 hrs. tempering was obtained at 850 deg. F. with each of the three quenched alloys. Conductivity test bars were then quenched from 1650 deg. F. and aged 24 hrs., at 850 deg. F. The results of the tests on these bars are given in Table I.

Table I.—Hardness and Conductivity of Copper-Zirconium Alloys.

Heat No.	Zirconium Content	Hardness, Rockwell E			Conductivity, Per Cent		
		As Cast	Quenched	Tempered	As Cast	Quenched	Tempered
61	1.45	64.5	53	76	61.1	56.7	75.5
63	2.4	73	65	79.5	55.0	50.0	68.0
64	3.24	76.5	71	84.5	44.0	41.2	55.0

Thus with increasing zirconium content there occurred an increase in hardness after tempering, and a corresponding decrease in conductivity; and in each alloy both hardness and conductivity were improved by tempering after quenching. While the maximum hardness obtained in this series was somewhat disappointing, the combination of hardness and conductivity was of interest.

Beryllium-Zirconium-Copper Alloys

Since an appreciable hardening occurred on tempering these alloys, and since zirconium is much less costly than beryllium, it was thought that the combination of zirconium and beryllium in copper might offer some advantage over the straight beryllium-copper alloy. Accordingly, some copper melts were made in which beryllium and zirconium were incorporated. The compositions of these alloys are given in Table II.

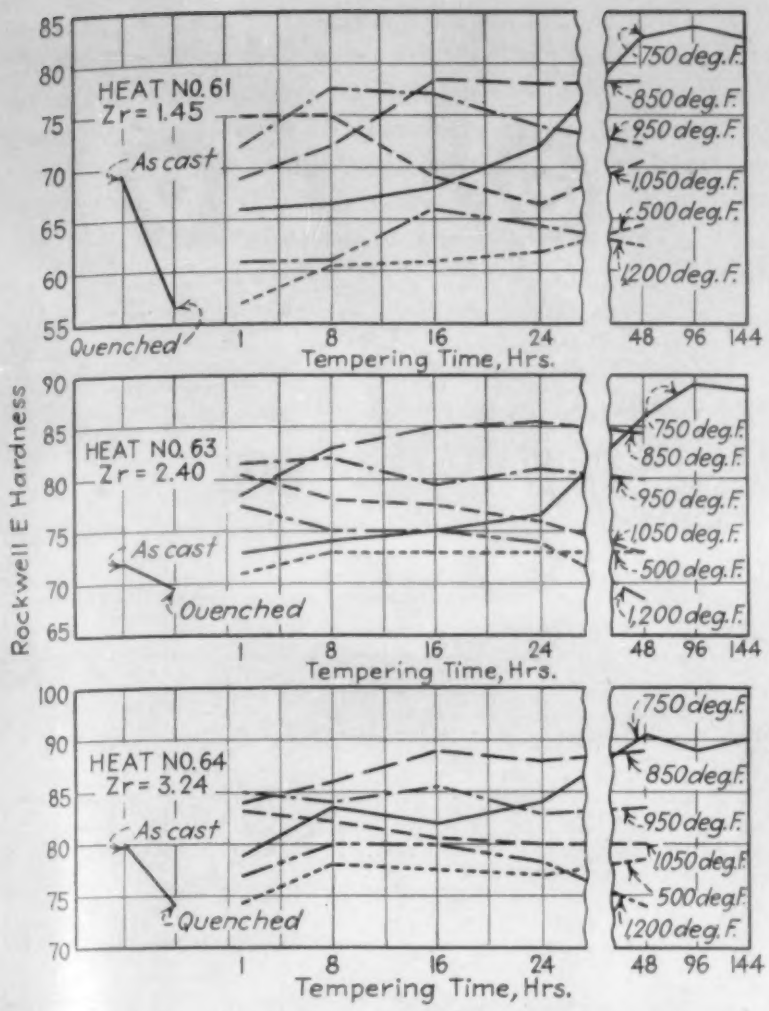


Fig. 1.—Hardness of Cu-Zr Alloys after Heating for Various Periods at Different Temperatures.

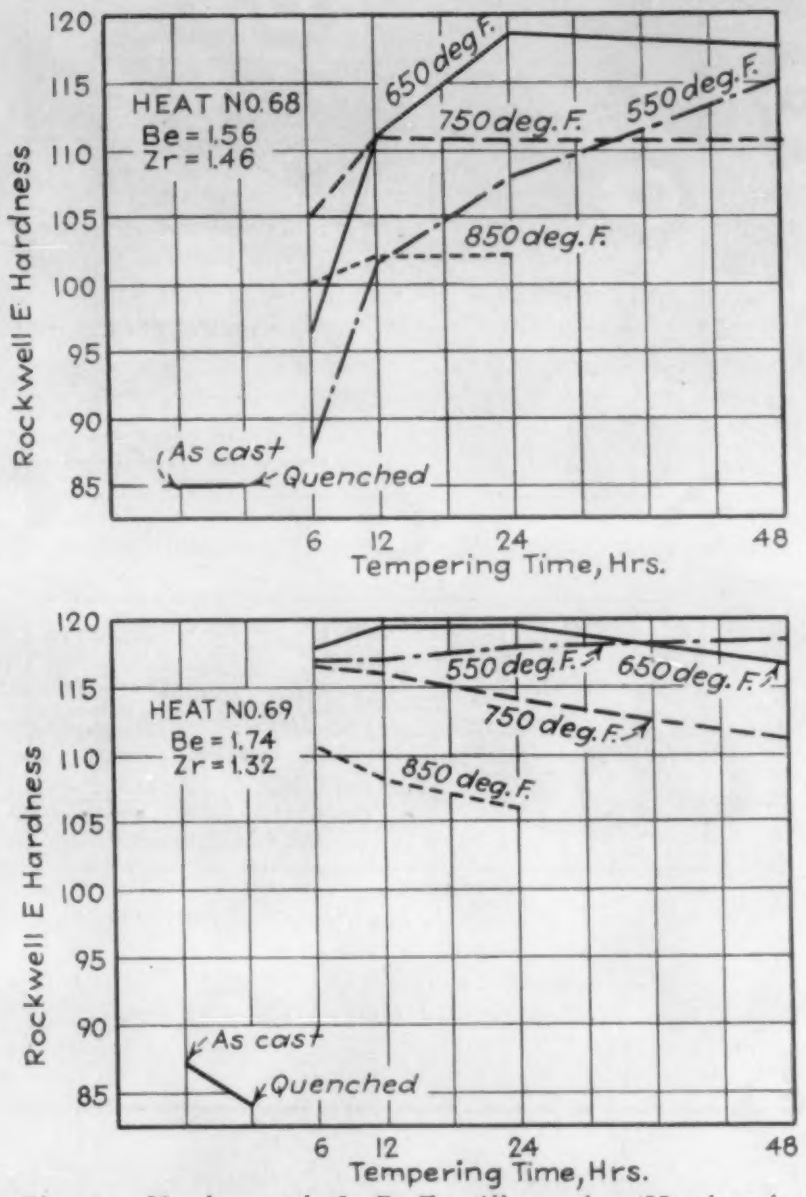


Fig. 2.—Hardness of Cu-Be-Zr Alloys after Heating for Various Periods at Different Temperatures.

Table II.—Analyses of Copper—Beryllium—Zirconium Alloys.

Heat No.	Beryllium	Zirconium	Iron	Titanium
68	1.56	1.46	0.061	Nil.
69	1.74	1.32	0.092	0.019
70	1.49	2.98	0.070	Nil.
71	0.81	2.70	0.057	....
72	1.14	3.52	0.076	....
73	1.92	1.36	0.109	....

These heats were melted as described above, except that a charcoal cover was used instead of glass. The beryllium was added in the form of a 4 per cent alloy after the copper was melted but before the zirconium, and almost perfect recovery was obtained.

The preliminary quenching and tempering experiments were performed with the first four of these heats. The heat treatment program was as follows: Water-quench from 1500 deg. F. and temper at 550, 650, 750 and 850 deg. F. for 6, 12, 24 and 48 hrs. respectively at each temperature with the exception that the 48-hr. treatment at 850 deg. F. was not used. The hardness variations in this series of samples are shown in Figs. 2 and 3.

After 24 hrs. tempering the maximum hardness was obtained at 650 deg. F. for two of the four heats, and at 750 deg. F. for the other two, although for one of these latter heats (No. 71) 650 and 750 deg. F. gave practically the same results.

After 48 hrs. tempering, the maximum hardness was obtained at 650 deg. F. for two of the heats, at 750 deg. F. for one heat (although 650 deg. F. gave practically the same figure), and at 550 deg. F. for the other heat (although again the hardness obtained at 650 deg F. was practically the same).

It was therefore decided that 650 deg. F. would be the best tempering temperature in general. Conductivity test bars from 5 of these heats (omitting No. 71) were tempered 48 hrs. at this temperature without preliminary quenching. The electrical conductivity and Rockwell E hardness were determined on each bar, after which they were quenched from 1500 deg. F. and tempered 48 hrs. at 650 deg. F. The results of these tests are shown in Table III.

Table III.—Hardness and Conductivity of Copper—Beryllium—Zirconium Alloys.

			Hardness, Rockwell E				Conductivity, Per Cent			
Heat No.	Zr	Be	As Cast	Tempered, no preliminary quenching	Quenched	Quenched and tempered	As Cast	Tempered, no preliminary quenching	Quenched	Quenched and tempered
68	1.46	1.56	85	113	82	116½	21.8	31.2	20.8	36.2
69	1.32	1.74	87	116½	79	116½	19.2	28.3	17.7	31.2
70	2.98	1.49	88	109	86	115	20.6	25.4	19.8	29.1
72	3.52	1.14	85	92	85½	96	22.6	24.1	21.7	23.7
73	1.36	1.92	85	119	78	119½	18.1	27.0	15.8	30.5

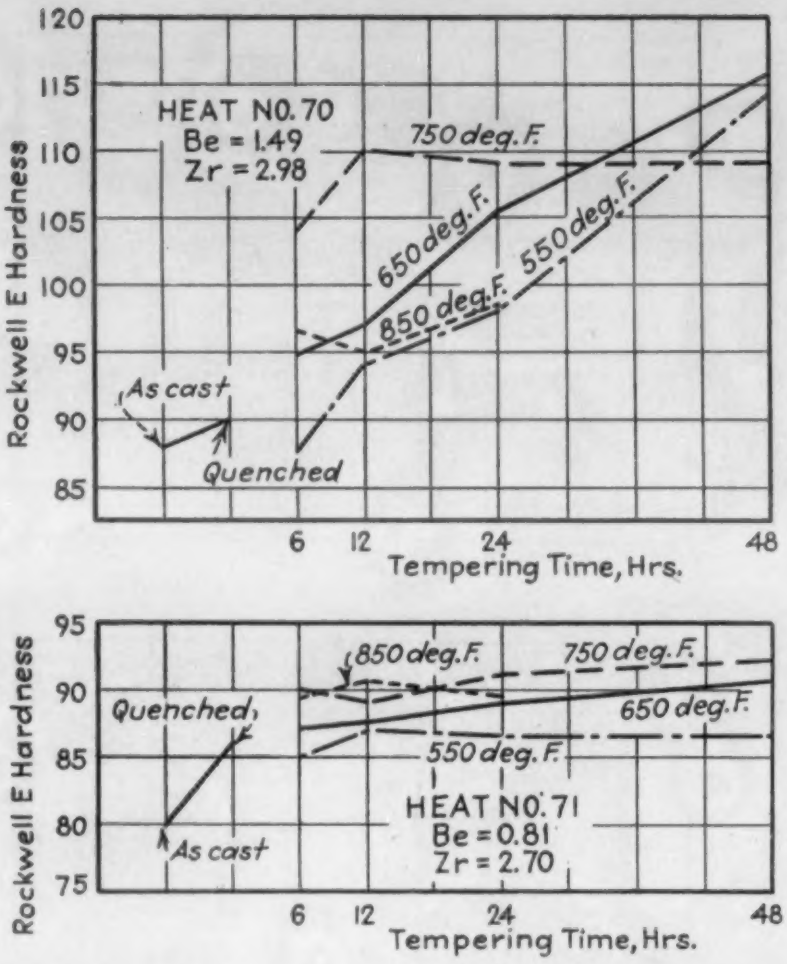
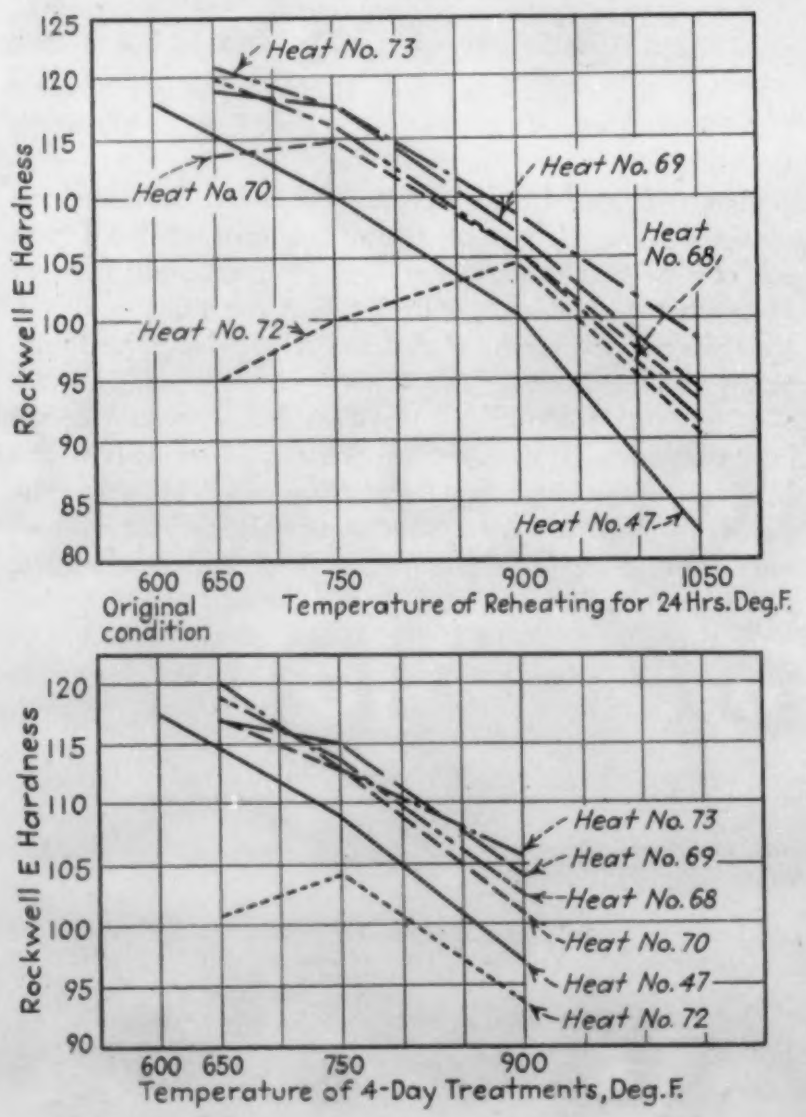


Fig. 3.—Hardness of Cu-Be-Zr Alloys after Heating for Various Periods at Different Temperatures.

Fig. 4.—Hardness of Hardened Cu-Be-Zr Alloys After Reheating.



In Table IV are shown the results of tests on two heats of beryllium-copper, for comparison with those in Table III. These heats had been made at an earlier date and data for exact comparison are lacking. They were melted under charcoal like the other beryllium alloys.

Table IV.—Hardness and Conductivity of Copper—Beryllium Alloys.

			Conductivity, Per Cent			
Heat No.	Be	Hardness, Rockwell E quenched and tempered	As Cast	Quenched from 1475 deg. F.	Tempered 5 hrs. 700 deg. F.	Quenched—1550 deg. F. Tempered 48 hrs. at 600 deg. F.
27	2.04	118	22.0	19.5	32.8	...
47	1.52	116½	...	...	...	36.1

From these results there does not seem to be much advantage in the use of zirconium in conjunction with beryllium, since neither the hardness nor the conductivity was appreciably improved. This is especially evident in heats Nos. 47 and 68, where the addition of about 1.50 per cent zirconium had no apparent effect on the properties. In heat No. 70, the addition of about 3 per cent zirconium gave a slightly lower hardness value and reduced the conductivity appreciably. With the zirconium content increased to 3.50 per cent, as in heat No. 72, both hardness and conductivity were decidedly lower, but the reduction in hardness can be accounted for by the lower beryllium content (1.14 per cent) of heat No. 72. It was only in heat No. 73 that the hardness was higher than without zirconium, and the beryllium content of this alloy was nearly as high as in heat No. 27.

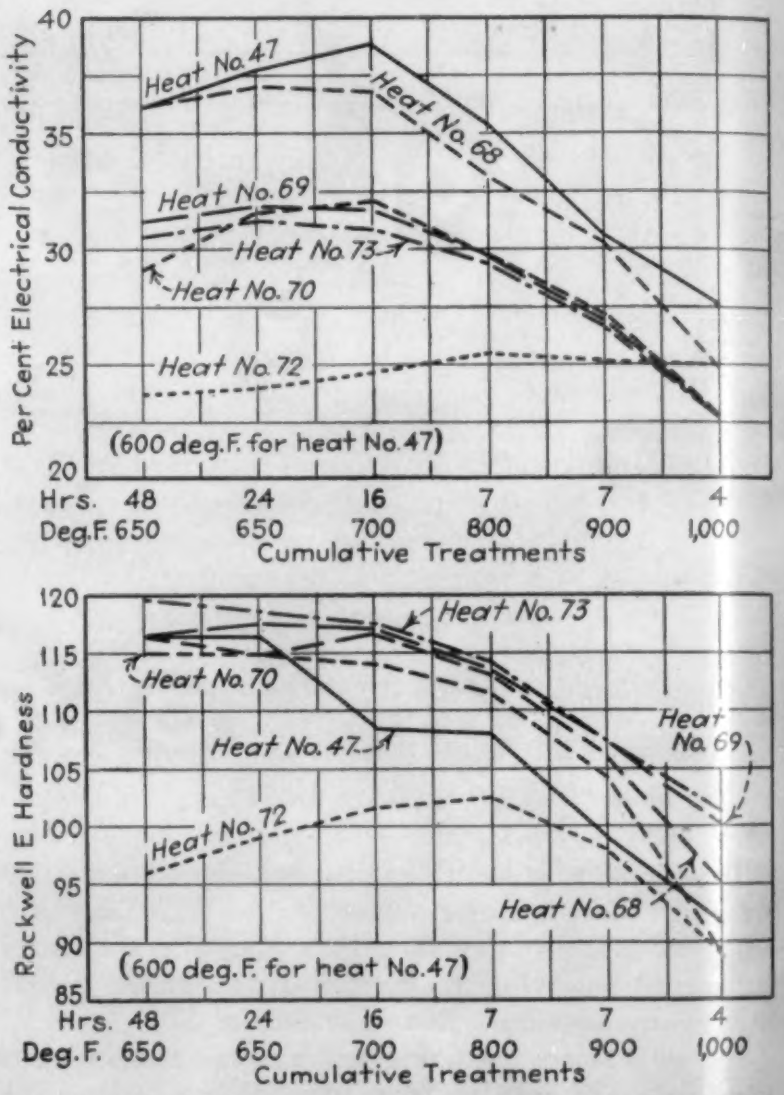

Heat No. 47
Heat No. 68
Heat No. 69
Heat No. 73
Heat No. 70
Heat No. 72
(600 deg. F. for heat No. 47)
Per Cent Electrical Conductivity
Hrs. 48 24 16 7 7 4
Deg. F. 650 650 700 800 900 1,000
Cumulative Treatments
Heat No. 73
Heat No. 70
Heat No. 47
Heat No. 69
Heat No. 72
Heat No. 68
(600 deg. F. for heat No. 47)
Rockwell E Hardness
Hrs. 48 24 16 7 7 4
Deg. F. 650 650 700 800 900 1,000
Cumulative Treatments

Fig. 5.—Conductivity and Hardness of Hardened Cu-Be-Zr Alloys After Various Consecutive Heat Treatments.

Zr and the Aging of Cu-Be Alloys

A series of heat treatments was carried out to determine to what extent, if any, zirconium improved the copper-beryllium alloys with respect to over-aging. Samples from the heats shown in Table III were hardened by quenching from 1500 deg. F. and then tempering for 48 hrs. at 650 deg. F. They were then subjected to the treatments shown in Table V. Heat No. 47 (without zirconium) is included for comparison.

Table V.—Rockwell E Hardness of Hardened Alloys after Reheating.

Heat No.	47	68	69	70	72	73
Original (48 hrs. at 650 deg. F.)*	118	120	119	113.5	95	121
After 4 days at 650 deg. F.**	117.5	119	117	117	101	120
After 1 day at 750 deg. F.	110	116	117.5	114.5	100	117.5
After 4 days at 750 deg. F.	109	113.5	115	113	104	113
After 1 day at 900 deg. F.	100	105.5	107	105.5	104.5	108.5
After 4 days at 900 deg. F.	97	102.5	104	101	103.5	105.5
After 1 day at 1050 deg. F.	82	91.5	94	93	90.5	98

* 24 hrs. at 600 deg. F. for heat No. 47.
** 600 deg. F. for heat No. 47.

Here it is apparent that the zirconium was of value. In every alloy containing zirconium the hardness was decreased less at the higher temperatures than in heat No. 47, without zirconium. In the case of heat No. 72 with 3.5 per cent zirconium the initial hardness was increased and then maintained even after 4 days at 900 deg. F. These results are also shown plotted in Fig. IV. The fact that the original hardness of heats Nos 68, 69 and 73 was found to be a little higher than that of heat No. 47 shows that zirconium did have a slight hardening effect in this series, although some of these differences may probably be ascribed to variations in the beryllium contents.

Similar over-aging treatments were given to conductivity test bars from these heats and the Rockwell E hardness values and electrical conductivity determined after each treatment. The results are shown in Table VI and Fig. 5. The various heat treatments were carried out consecutively and the results are therefore cumulative. Heat No. 27 (without zirconium) is also included in Table VI to offer further comparison.

As in Table V, it is again evident that, in the alloys containing zirconium, the hardness was maintained better at the higher temperatures. However, this beneficial effect was not found with respect to the conductivity. After heating at the higher temperatures, the conductivity was less in the alloys with zirconium than in the plain beryllium copper. From this it is evident that the precipitated phase must be re-dissolved on over-heating the alloys containing zirconium the same as it is in the plain beryllium-copper. The retardation of softening by the zirconium may be due to a prevention of growth of the precipitated particles which are too large to be rapidly dissolved at the temperatures used for over-heating, and yet not above the critical size for hardening. Or a zirconium compound may be growing, during the over-heating, from a sub-critical to an effective hardening size, thus tending to maintain the hardness, while a beryllium compound is passing into solution and reducing both hardness and conductivity.

Table VI.—Hardness and Conductivity after Various Consecutive Heat-Treatments.

Heat No.	27	47	68	69	70	72	73
Beryllium content	2.04	1.52	1.56	1.74	1.49	1.14	1.92
Zirconium content	0	0	1.46	1.32	2.98	3.52	1.36
Electrical conductivity, per cent							
Quenched and tempered 48 hrs. at 650 deg. F.	29.0*	36.1†	36.2	31.2	29.1	23.7	30.5
Tempered 24 hrs. more at 650 deg. F.		37.8†	37.1	31.8	31.5	24.0	31.2
Tempered 16 hrs. more at 700 deg. F.	36.8‡	38.8	36.8	31.7	32.0	24.6	30.8
Tempered 7 hrs. more at 800 deg. F.		35.4	33.1	29.6	29.7	25.4	29.3
Tempered 7 hrs. more at 900 deg. F.		30.6	30.2	26.8	27.0	25.2	26.6
Tempered 4 hrs. more at 1000 deg. F.		27.6	24.8	22.6	22.6	24.8	22.8
Rockwell E hardness							
Quenched and tempered 48 hrs. at 650 deg. F.	120 *	116.5†	116.5	116.5	115	96	119.5
Tempered 24 hrs. more at 650 deg. F.		116.5†	115	117.5	115	99	118.5
Tempered 16 hrs. more at 700 deg. F.	115 ‡	108.5	116.5	117	114	101.5	117.5
Tempered 7 hrs. more at 800 deg. F.		108	113	113.5	111.5	102.5	114
Tempered 7 hrs. more at 900 deg. F.		99	106	107	104	98	107
Tempered 4 hrs. more at 1000 deg. F.		91.5	95	100	89	89	101

* 9 hrs. † 600 deg. F. ‡ 35 hrs. total.

The results of this investigation show that the alloys of copper and zirconium are of interest because of their high electrical conductivity, especially after suitable heat treatment. When used in conjunction with beryllium, zirconium increases the hardness very slightly, but diminishes the degree of softening at temperatures high enough to affect seriously the hardness of heat-treated beryllium copper.

The authors acknowledge with thanks the efficient assistance of V. V. Efimoff and A. Yocco in preparing the alloys for this work, and also appreciate the facilities provided by the Titanium Alloy Mfg. Co., for making the tests and their permission to publish the results.

Photo by H. W. Fortey, The Warner & Swasey Co., Cleveland

Typical Scene in an American Iron Foundry

PRODUCTION DATA OF THE

Steel Foundry Industry

by Edwin F. Cone

STATISTICAL data may be regarded as weather vanes of an industry. Properly interpreted, they are of considerable value. This is particularly true of the steel industry as a whole, as well as of certain branches of it. So far as steel ingots and rolled products are concerned, the data of the American Iron and Steel Institute, as at present published, are quite complete and accurate.

No Data Since 1933

When it comes to the foundry industry, an entirely different situation exists. Previous to the NRA and the establishing of Codes of Fair Practice, the Institute collected and published production data of the steel foundry industry, broken down fairly completely into melting processes and types of castings, i.e., whether open-hearth (basic or acid), electric furnace, converter and crucible and whether plain carbon or alloy steels. With the coming of the Codes, this complete and satisfactory service was stopped.

Therefore, whereas up to and including 1933 we had for reference rather complete information concerning the steel foundry industry as a whole, today such published data are not available. The earlier statistics referred to included not only commercial or jobbing foundry production of plain carbon and alloy steel castings, but also castings made by producers for their own use. The data for alloy steel castings took in all the ordinary varieties of the lower alloyed products, most of the manganese steel castings and some of the high alloy or stainless steel (Cr and Cr-Ni) castings. Today none of this information, as officially assembled, is published and some of it is not available at all. This is regarded by many as unfortunate and regrettable.

Previous to the Codes and in addition to the American

Pouring Cast Steel Crankshafts in the Rouge Plant of the Ford Motor Co. (Courtesy: Ford Motor Co.)

Pouring a Steel Casting in an American Open-Hearth Steel Foundry. (Courtesy: Climax Molybdenum Co.)

Iron and Steel Institute, there were in existence the American Foundrymen's Association and the Steel Founders' Society of America, the former a technical organization and the latter a trade association. They did not collect production data. Both these associations continue to function today and are highly important to the foundry industry within their respective fields of activity. But there has been a split-up, as a result of the New Deal, of the extent to which the Steel Founders' Society of America embraces the industry. This society now has for its members only those steel foundries which produce miscellaneous and special commercial castings for sale in the open market, including all plain carbon steels and most of the low-alloy compositions. It does not include the high-alloy or so-called stainless steel casting producers, nor the manganese or Hadfield steel foundries. It does now, however, collect rather complete data of the production of its members. This is claimed to represent about 95 per cent of the total output of miscellaneous and special commercial castings for sale in the open market.

The Stainless Steel Data

The situation as to the stainless steel or high-alloy producers of chromium and chromium-nickel alloys is as follows: Under the Codes the Alloy Casting Association was organized. It still exists and functions and has as its members most of the producers of such products. This trade association does collect statistics of the output which probably represent over 95 per cent of the total produced. These data, however, are not available for publication or even consultation—they are closely guarded. The reason offered is that the members do not desire the expansion of the industry to be known because such information might induce competition from present non-producers. It is the policy of this association to forbid its members to give the data to any one seeking them.

Output of Manganese Castings

As to manganese steel castings (12 to 14% Mn)—for a brief period, about six months, the producers did belong to the Steel Founders' Society of America but, when the Supreme Court killed the NRA, they withdrew. Today these producers have a trade association called the Manganese Steel Founders' Society. The writer does not know whether this organization collects production data nor, if it does, whether they are available for public scrutiny.

Summing up then, the situation as to production statistics of the entire steel foundry industry is that the American Iron and Steel Institute no longer gathers such information; that the Steel Founders' Society of America, which

represents about 95 per cent of the producers of miscellaneous and special commercial steel castings, does collect the data of total output non-segregated and not including castings made for own use; that the Alloy Casting Association assembles data covering high alloy or stainless steel production but jealously treasures them; and that the Manganese Steel Founders' Society may collect them, or may not. Thus it is evident that complete data of the steel foundry industry as a whole are not available.

Production Data for Last Three Years

Through the courtesy of the Steel Founders' Society of America, the writer is able to publish that organization's production data for the past three years—1934, 1935 and 1936. These data are here presented in three different calculations: (1) Total data as collected by the Society; (2) estimated output of all producers of the Society representing 95 per cent of the total miscellaneous and special commercial castings; and (3) the estimated production of the foregoing plus the output of those companies which produce castings for their own use, such as the large machinery builders, the electric companies and some of the large steel companies. This figure is arrived at on the basis that the data represented by (1) and (2) are 83 per cent of the country's total, as arrived at by the experience of the Steel Founders' Society over a period of years. On this basis the data are given in Table I.

Table I.—Output of Miscellaneous and Special Commercial Steel Castings in Net Tons

	S.F.S.A.	Total *	Including Castings for Use *
1934	375,122	395,000	476,000
1935	368,851	388,200	467,700
1936	718,068	755,800	910,000

* Estimated.

Thus in 1936 the American production of miscellaneous and special commercial steel castings was 755,800 net tons. And the country's total, including the castings made by companies for their own use and not for sale in the market, was 910,000. The data reveal the remarkable recovery which has taken place last year. The 1936 production of 718,068 tons represents an increase of 91.4 per cent over the 1934 output. At the end of January the industry was operating at 83.1 per cent of capacity.

Situation as to Alloy Steels

One regrettable feature of these data is that there is no segregation as to alloy steel production such as were obtainable from the American Iron and Steel Institute. The data previous to 1934, as presented by the Institute, are given in Table II.

Table II.—American Steel Casting Production in Gross Tons

	Castings	Alloy	Alloy Per Cent
1921	559,713	40,255	7.2
1926	1,357,558	146,101	10.7
1929	1,583,040	192,920	12.2
1930	1,104,215	126,128	11.5
1931	516,579	89,903	17.4
1932	216,760	41,044	18.8
1933	338,061	71,783	21.2
1934	425,000 *	.....	...
1935	417,600 *	.....	...
1936	812,500 *	.....	...

* Steel Founders' Data in Column 3 in Table I in gross tons.

The data in Table II show that the 1936 steel casting production of at least 812,500 gross tons, based on the Steel Founders' Society data has swung back to above the 1931 output. On the basis of the alloy steel casting percentages, which were constantly increasing up to 1934, it is a fair assumption that in 1936 this total was close to 25 per cent of the total, or over 200,000 tons, which exceeds the 1929 peak production.

Tapping a Large Heroult Electric Arc Furnace. A large tonnage of alloy steels is made in electric furnaces.

Estimates of 1936 Totals

Some interesting data on the production of the United States of all types of castings for 1936 are possible by calculation. Taking the figures of the Steel Founders' Society of America as a basis and estimating the stainless steel and manganese steel castings output, the following table is arrived at in net tons:

Misc. and Special Com.	755,800
For Companies' Own Use	154,200
Manganese	50,000
Stainless or High Alloy	5,000
Total	965,000

Figured to gross tons this total of 965,000 net tons is approximately 861,600 tons which compares roughly with the 812,500 gross tons in Table II. The discrepancy is due to data not included in the Steel Founders' Society figures.

These data, as analyzed in the preceding paragraphs, are interesting as showing at least the trend of the steel foundry industry. It is unfortunate that there are now no data covering alloy steel castings of any type. The growing importance of alloy products warrants a plea that this information be made available, and it is hoped that this may soon be realized—including stainless and manganese steel.

Steel Reminiscences—IV

(Continued from Previous Three Issues)

by Henry D. Hibbard

Consulting Engineer, Plainfield, N. J.

FROM 1886 TO 1890, at the Linden Steel Works, long since absorbed by Jones & Laughlin Steel Co., I had a varied experience. Boiler and ship plate as well as spring and machinery steel were made there.

The plate mill had two stands of rolls, two-high, though the plates were rolled at one heat from ingot to finished plate. We had an order for the protective deck and engine hatchway armor plate for the new cruisers for the navy. They were from 1 in. to 4 in. thick. To handle these in rolling, as the ingots for them were much larger than had been made there before, tables with driven rollers were needed for the plate mill. With some help from the president of the company I designed and drew them. They worked successfully.

Later, when I had charge of the steel shop, I made, on that order, the steel for the first American steel armor ever to be struck by a hostile shot. It was the protective deck of the cruiser Baltimore. In the battle of Manila, a Spanish 6-in. shot came aboard but was deflected by the armor, which was not penetrated. It hurt no one and did but little damage. Its course through the ship was explained to me by Lieutenant Rodman, now Admiral Rodman, retired, when he returned to New York on the Raleigh, which was the first of Dewey's fleet to reach that port.

An Early 20-Ton Open-Hearth

I designed and built there a 20-ton siema after the general though bad plan then popular. It had a circular hearth, which was set low, with regenerators located under the charging floor. As a result of the lack of sufficient vertical height of that arrangement, the air for combustion did not flow freely enough to the working chamber through the regenerators and too much entered through cracks in the brickwork and around the doors.

To correct this I installed a fan blower to blow the air—the first time a siema was so equipped anywhere. That enabled me, as both gas and air entered the laboratory of the furnace under pressure, to maintain a slight plenum within, which prevented cold air entering. Such a plenum not only expedited the operation, increasing the efficiency of the furnace, but lessened the waste of the charge materials during melting.

Rimming or Effervescing Steel

At Linden I first recognized rimming steel as a distinct variety, which I then called "effervescing" steel because of the gas which escapes from it while cooling and freezing in the mold. Also I learned the use of ore to eliminate carbon, and the evil effects of a too high casting temperature in the metal, especially for rimmed steel, and how to avoid it. I installed my quick test methods and taught my melters to do them.

First Use of Aluminum as Fe-Al

My first use of aluminum added to steel to kill it was made there too. Hall had not then invented his method of making aluminum metal. What I used was an iron-aluminum alloy, made by Cowles of Cleveland, Ohio, containing about 10 per cent aluminum. It was made in a resistance electric furnace. Because of the high temperature, Cowles problem was to preserve the aluminum after it was reduced by carbon from its oxide by the high heat. So he provided a supply of iron to take it up and alloy with it. The aluminum in his alloy, as I recall it, seemed to have about the same killing effect on the steel as the same quantity of the metal in its unalloyed form. Natural gas was almost the sole fuel used for melting and working steel at Linden. It is wonderfully fine for such purposes.

At Linden I had my first experience with silica in acid steel and its harmful effects, though I have referred to an experiment in that field which failed. Our ship plate was passing inspection, in a way, with narrow margins but the surfaces were not good because of scale rolled in. The only unusual thing in the composition was high silicon, from 0.02 to 0.03 per cent. Thinking the trouble was due to that silicon, I tried to get rid of it by oxidizing it more completely in later heats by larger additions of ore, but to my astonishment that resulted in higher silicon in the finished steel and the quality was worse instead of better. Then it dawned on me that what the chemist reported as silicon was probably its oxide in the metal.

These heats had no residual manganese at the end before the final additions were made. To eliminate the SiO_2, a base was manifestly needed, or, specifically, oxide of manganese. To provide that oxide I added to the bath metal, some time before tapping, enough spiegel to give the metal 0.05 per cent manganese, which improved the quality notably and at once. Physical properties, especially ductility, of later heats were better, and scale came off in rolling in large sheets leaving clean and smooth metal surfaces.

Early Attempts to Make Basic Steel

At Linden in 1889 I first made basic siema steel. We

got some Spaeter magnesite from Austria to make the bottom. Suitable pig iron was not to be had as that available had near 3 per cent of sand sticking to it. Fluorspar was not known as a suitable flux for the slag, or procurable if it had been. So I had plenty of trouble with the furnace bottom. It got out of shape and I could cut down protuberances only with sand which was a bad thing to use. So after about six weeks' run, the furnace was changed back to an acid hearth. The basic steel was generally good however.

The next time I made basic steel, at the Crescent Steel Works, Pittsburgh, in 1890, I melted the sand-cast pig in another furnace and ran it out on iron plates just to clean it of sand. It worked well. In 1893 I wrote a paper for the Iron and Steel Institute of England on "Sand on Pig Iron" in the basic process, the trouble it caused and its avoidance. Six months later the Carnegie Steel Co., at the Lucy furnaces, were making sand-free machine cast pig iron.

To my first heat of basic steel, not knowing any better, I added ore as freely as to an acid heat. It was low carbon steel, and it effervesced so strongly in the bottom-cast molds that, after they were filled, the steel settled to about half the height and weight. That taught me that ore is more effective in basic than in acid siema processes. Less was needed. The right amount was soon learned.

Reversion of Manganese from the Slag

One thing which astonished me in that basic steel run was the reversion of manganese from the slag to the metal during the working period, which I never encountered in acid steel. In the basic bath metal, after manganese had been completely eliminated, later samples showed one or two points of that element, though none had been added. The charge and slag were both low in manganese compared with present practice. The average of the charge was perhaps not over 0.40 per cent or at most 0.50 per cent manganese, most of which, if not all, was oxidized during melting, and was therefore in the slag.

Others, I believe, have found some reversion of manganese to take place in the acid process, in high quality, high carbon heats, held for a long time in the furnace after any ore additions.

At a certain basic open-hearth steel works in England, which I visited in 1923, no fluorspar was added to the slag which was high in phosphorus or around 15 per cent P_2O_5. The omission of fluorspar was due partly to its cost, but more because slag containing it would not be valuable as a fertilizer for agriculture. The return from the sale of slag was essential to continued operation of the plant. I assumed, without knowing, that phosphate of calcium was fusible enough to contribute to keep the slag fairly fluid, which it was. *(To be concluded)*

A NOTE ON THE Mounting of Specimens in Bakelite

by J. L. Everhart

U. S. Metals Refining Co., Carteret, N. J.

TWO YEARS AGO, H. M. Schleicher and the writer[1] published an article on the mounting of specimens in bakelite. The method required only very simple equipment and was especially suited to those laboratories where the expense of a mounting press was not warranted. The only disadvantage of the process was the length of time required to harden the mounts.

Recently, H. J. Taffs[2] published an article in which he described the mounting of tin alloys in a bakelite resin to which an acid hardener was added. The material was hardened by heating to 45 deg. C. for ½ hr. and to 65 deg. C. for 1½ to 2 hrs. We have experimented with the method as applied to copper and steel and find that, with a slight modification, the mounts obtained are very satisfactory.

The materials used are "Bakelite Resin XR-3220," "Bakelite Hardener XK-2997," both obtained from the Bakelite Corp. and "Bakelite Varnish S.D. 17" obtained from John W. Masury & Son.

Method

The specimen to be mounted is covered with bakelite varnish, either by dipping or brushing, and dried. The drying may be accomplished by placing the specimen in the heating apparatus at 45 deg. C. for from 10 to 15 mins.

The bakelite resin is prepared for use by the addition of from 10 to 20 per cent by volume of the hardener when ready to make the mounts. The two materials must be thoroughly mixed in order to obtain a satisfactory mount, the mixing being done preferably in a vessel other than that in which the mount is to be made as it has been found that the bottom of the mount has a tendency to soft spots if the mixing and mounting are done in the same cup, due probably to lack of complete mixing at the extreme bottom. The mounting cups, containing the samples and bakelite mixture, are placed in an oven at 40 to 45 deg. C. for ½ hr. and the temperature is then raised to 65 to 70 deg. C. for from 1½ to 2 hrs. after which treatment, the mounts are fully hardened. No difficulty has been experienced in getting the mounts out of the cups even though no grease is used.

For very small copper wires, it is possible to obtain good mounts without coating the wire with varnish; however, for larger copper specimens and for all steel samples, the varnish must be used as, otherwise, the bakelite has a tendency to shrink away from the specimen.

Details of the mounting methods and the oven used were given in the previous paper, the only changes necessary being the alteration of the oven for use at 40 to 45 deg. C. and 65 to 70 deg. C. instead of the temperature ranges previously mentioned.

References

(1) Schleicher and Everhart, METALS AND ALLOYS, Vol. 5, 1934, pages 59-60.

(2) Taffs, *Journal* Royal Microscopical Society, Vol. 56, 1936, pages 300-306.

A Few CHUCKLES

A Tabloid Paragraph for Busy Executives!

We thank N. L. Mochel for calling our attention to a paragraph in one of the services that record commercial developments in tabloid paragraphs for the busy executive. This refers to a "new" Cr-Ni alloys that resists creep under load at high temperature. It is as follows:

> Tensile strength, after heating to 1800 deg. F. and holding for 1000 hrs. is 75,000 to 85,000 lbs. per sq. in. Creep is 1 per cent in 10,000 hrs. at the same high temperature.

Apparently the busy executive isn't supposed to care about short time tensile strength at high temperature or about what load will produce 1 per cent creep.—H. W. G.

Why Not Say What Is Meant?

Time for Feb. 15, 1937, page 36, says: "A new stainless alloy, containing 2 per cent white glass, will be used for the sheets forming the statue."

If *Time* means sheets coated with colorless enamel, why not say so?—H.W.G.

Chuckle or Groan?!

This is no Chuckle—It's another groan: "Steel will crystallize slowly from continual bending around sheaves."—*Sat. Ev. Post,* March 6, 1937, page 100.—H.W.G.

Both Real Live Men!

From the program announcement of the New York Chapter of the A.S.M. for March—

"Both the speaker and technical chairman are too well known to need any *obituary.*" (Italics ours.)

The speaker was E. E. Thum and the technical chairman Dr. A. B. Kinzel. This glaring error was not intentional—it was poor chirography and proof reading!—E.F.C.

Tetrium

We are indebted to C. E. MacQuigg for the following extract from a letter describing a product emanating from Burbank, Cal.:

> "Tetralloy gets its name from the Latin word Tetra—meaning four. The four elements are—nickel, gallium and iridium totaling less than 1 per cent and tetrium in excess of 99 per cent. Tetrium in the pure state is a transparent crystal, one millimeter in width and several millimeters in length, has a hardness approaching the diamond, and is insoluble in any known combination of solvents. This last named characteristic has been the stumbling block that has caused several noted chemists to independently report such erroneous analyses as FeC_2 (not FeC_3); CSi; 24% Zn; etc. Tetrium, the newly discovered element, places itself as number 98 in the periodic system of elements."

The Burbank environment must favor the crossing of elements as well as plants.—H.W.G.

A LETTER TO THE EDITOR

Something New in Welding?!

To the Editor: We have enjoyed reading Highlights in METALS AND ALLOYS and frequently get a laugh out of "Chuckles."

A matter has been brought to our notice that seems worthy of your attention. According to the literature the salesman gave us:

> Cracked and leaking valve seats on automobile engines, cracked and leaking truck blocks, water leaks in the heaviest Diesel engine heads, cracks in heavy castiron boiler sections, and cracks in crankcases, either aluminum or cast iron, are now successfully Excelswelded.
>
> Excelswelding overcomes casting strains and seals the cracks all the way through regardless of the thickness of the metal. Excelswelding makes for increased thermal efficiency! *Expansion and contraction are overcome by the improved Excelsweld method.* Excelsweld jobs, done three years ago and in use every day, are still holding.
>
> No solution or sealing compound is used in the circulating system in the casting. Th Excelsweld bonding material, used in the cracks, can not be burned out or dislodged. *Cast iron that will no longer weld is easily Excelswelded.*

Evidently "Excelswelding" renders all other efforts to repair cast iron useless. The salesman told us that the material used has no tensile strength. Welding? Well, Well!

WAYNE A. HOWARD.

General Petroleum Co. of Cal.
Los Angeles, Cal.

We have always hoped that somebody would overcome expansion and contraction. *(Italics ours.)*—Editors.

METALS AND ALLOYS IN THE

Printing Industry—IV

by B. W. Gonser and S. Epstein

Battelle Memorial Institute, Columbus, Ohio

This is the fourth and last installment of a series on this subject. Part I was published in the January issue, Part II in February and Part III in March. The discussion is another in the series of articles on the general topic of the Metallurgical Needs of the Non-Metallurgical Industries.—Editor.

Photoengraving Plates

AT ONE time all photoengravings were made on zinc. Then a bicromatized glue was discovered which worked best on copper. This glue or "top" could be allowed to remain on the plates during printing, since it was baked hard or "burned in" before the plate was etched. Corrective re-etching was thereby made possible because of the practically permanent resist carried on the printing surface. Copper, therefore, became popular. Now there is a shellac resist called "cold top" because no heating is required, and this works equally well on copper or zinc. In general copper or brass gives a smoother surface than zinc and is preferred. Zinc is etched with a nitric acid solution which acts more rapidly than does ferric chloride on copper. This makes the etching of "deep-etched" plates somewhat easier on zinc. For plates to be soldered or backed up with electrotype metal, copper is preferred because of the relatively low melting point of zinc.

Zinc Plates

In making zinc sheets for photoengraving[13] slabs are cast in open molds. The bottom side of the casting being the best for the final plate, is kept identified throughout the rolling. After rolling to about 0.065 in. thickness the sheet is ground and polished on the good side to produce a finished surface free from flaws. Minor defects, such as tiny pits, scratches, small blisters, etc., which would not be considered objectionable in rolled zinc sheets for any ordinary use, must be entirely absent in photoengravers' plate, since any of these would probably cause trouble during etching.

The zinc sheet must contain a certain amount of lead and cadmium in order to have the proper strength, hardness, and etching properties. Approximately 0.3 per cent of each of these elements has a definitely beneficial effect in making the etching more uniform. They give a finer grain and smoother texture to the surface of the metal than is obtainable with pure zinc. Iron, on the other hand, is detrimental and should be kept below about 0.02 per cent. Iron forms a compound with zinc and if present above the amount stated may cause etching difficulties since the particles of the compound stand out in relief.

When the sheet as received from the manufacturer is cut into smaller sized plates, care must be taken, particularly in color work, to see that the rolling direction in each plate is the same. Otherwise differential expansions may occur during etching and heating, thus marring the register. A grade of hard rolled zinc is considered to be better for fine

Thickness Gage for Precision Measurement of Blocked Plates. (Courtesy: Hacker Mfg. Co.)

Type Gage. Used for rapidly measuring height of Linotype slugs and machine cast type. (Courtesy: Hacker Mfg. Co.)

Make-up Gage. This is something used for checking lateral dimension and unit position of assembled pages of type. (Courtesy: Hacker Mfg. Co.)

halftone dots, but it tends to warp and buckle. This can be overcome by straightening at about 200 deg. F.

Sheet Brass

The brass alloys used for photoengraving sheet have been given by McGar[14] as follows:

	Copper	Zinc
High brass	66	34
Low brass	80	20
Rich low brass	85	15
Commercial bronze	90	10

The impurities present are lead which is usually under 0.1 per cent and iron, below 0.05 per cent. After cold rolling, the sheet is bright annealed and polished without being pickled. For best etching results the grain structure should be uniform and the grain size approximately 0.025 mm. in diameter. The sheet is generally used in half-hard temper. It is, of course, necessary that the gage of photoengraving sheet should be uniform, in order to save work in bringing up the height of type face.

Lithographic and Gravure Plates

As has been explained, these plates are not etched, (deep

Pre-Makeready Equipment for Blocked Plates. A plate gage is used to measure accurately plate thickness, the block leveller shaves the block to desired thickness, and graduated underlay paper is pasted on the bottom of the blocks when necessary to adjust final height. (Courtesy: Hacker Mfg. Co.)

etched lithographic plates have about 0.001 or 0.002 in. depth as compared with several times that amount in the shallowest photoengravings) but serve merely to hold the photochemical gelatine. Thus the main requisite is good flexibility for curving around the printing cylinder and a smooth surface. The surface is "grained" with emery to hold the ink better. Either zinc or aluminum sheets are used. There is a possibility that low-carbon steel sheets would be suitable. The requisites are good flexibility, corrosion resistance to the ink and water used in printing, and availability in exact gage.

Gravure plates are made of copper. For rotogravure printing, large copper cylinders were formerly used which were machined, or ground and polished after use, to present a new surface. By occasionally electro-depositing a layer of copper onto the cylinder, compensation could be made for losses. Now, a method widely used is to electrodeposit a layer of copper onto a steel cylinder core and polish before etching. For very large cylinders, a seamless copper tube that may be pressed over the steel core has advantages. The suggestion has also been made to use copper or a copper alloy cast around a heated steel core to form a tightly bonded unit.

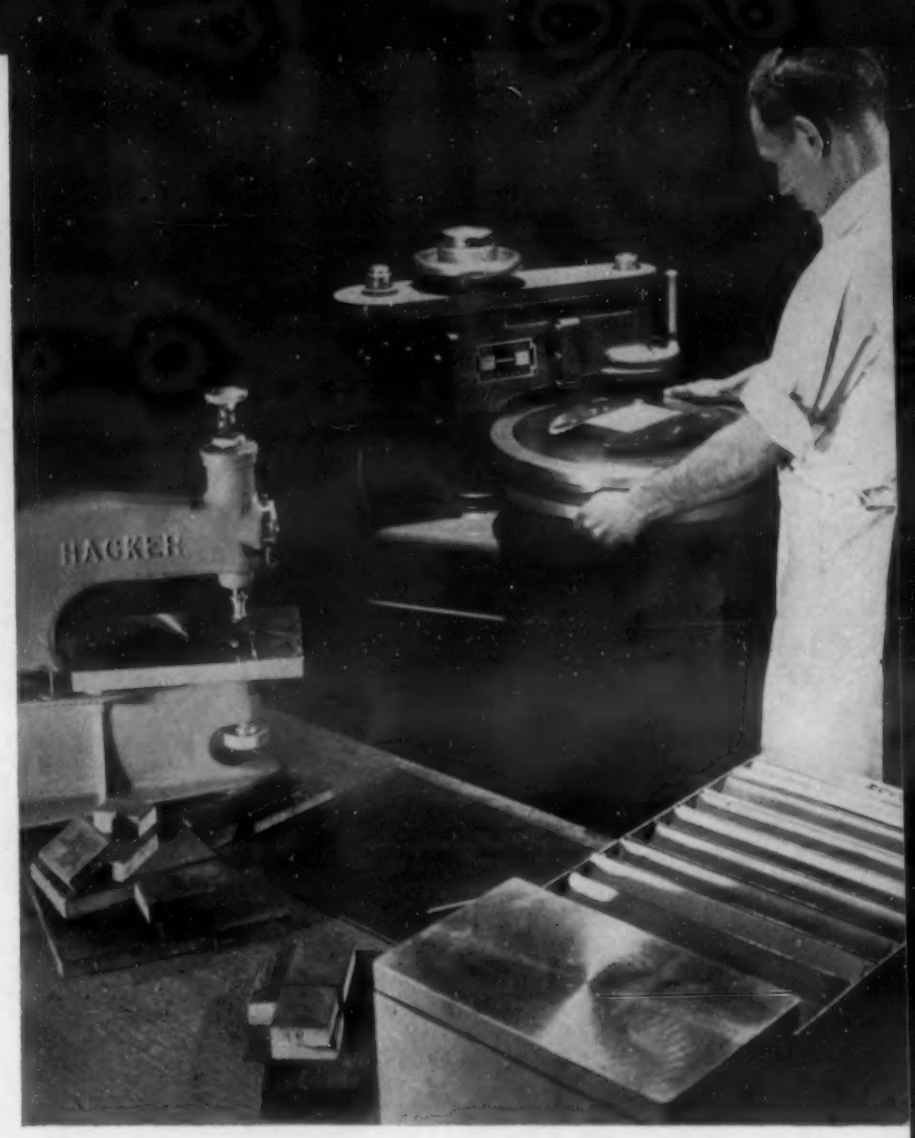
Steel Engraving Plates

In this method of reproduction an intaglio pattern is cut into a low-carbon steel plate which is then cyanide hardened. Printing can be done directly from this steel engraving, or else, for large editions, the original plate is used as a pattern plate for transferring the design onto another soft low-carbon steel plate. The latter is in turn cyanide hardened and used as a pattern plate for making any desired number of printing plates, these being molded while in the soft condition and then cyanide hardened. In recent years the life of intaglio plates has been greatly increased by chromium plating the surfaces. The principal requisite for steel plates for engraving is the absence of seams, slivers, and other surface defects.

Precision in Printing

The clarity and sharpness discernible in good printing obviously owes this quality to the use of metals, from the cutting and etching of the original type and halftones on through the different reproduction stages. Thus the important problem of precision in printing fits naturally into a discussion of metals in the printing industry.

To take letterpress printing as an example, the type and halftones on the printing plate must not only be properly cut, etched, molded, uniformly spaced, and made exact in size to get proper register, but all of the surfaces in relief must be in a proper printing plane to give a uniformly clear, sharp print, and to bring out the full tone values. These measurements and adjustments in the preparation and reproduction of the type and printing plates, and in the printing operation itself, can be made by the proper craftsmen with the aid of very few instruments, largely as a result of skill born of long experience. The final results obtainable by the application of such handicraft cut and try methods to large scale modern printing are truly remarkable. Nevertheless they are costly and the ideal of the "precisionists" in the printing industry to obtain equal or better results by the use of precision instruments, precision machines in making the type and plates, and precision printing presses, would produce a large saving in time consuming and expensive hand operations.



Another View of the Operation Shown in Preceding Illustration.

In discussing precision in printing it will be well to bear in mind the magnitude of the dimensions involved. That the difference between corresponding points should not be greater than 0.003 in. in order to secure accurate register in color half-tones has already been mentioned. For good printing value the departure from the proper type height of any part of the printing surface should not be over 0.001 in. Thus if the printing portions on any part of the plate are 0.001 in. under type heights, they will tend

A Block Leveller. This precision planer is used for accurately leve ling wood or metal blocked plates. (Courtesy: Hacker Mfg. Co

to print too lightly, and if they are 0.001 in. over there will be a tendency to excessive pressure. On the other hand, variations in height of less than 0.001 in. produce no discernible difference in printing value.

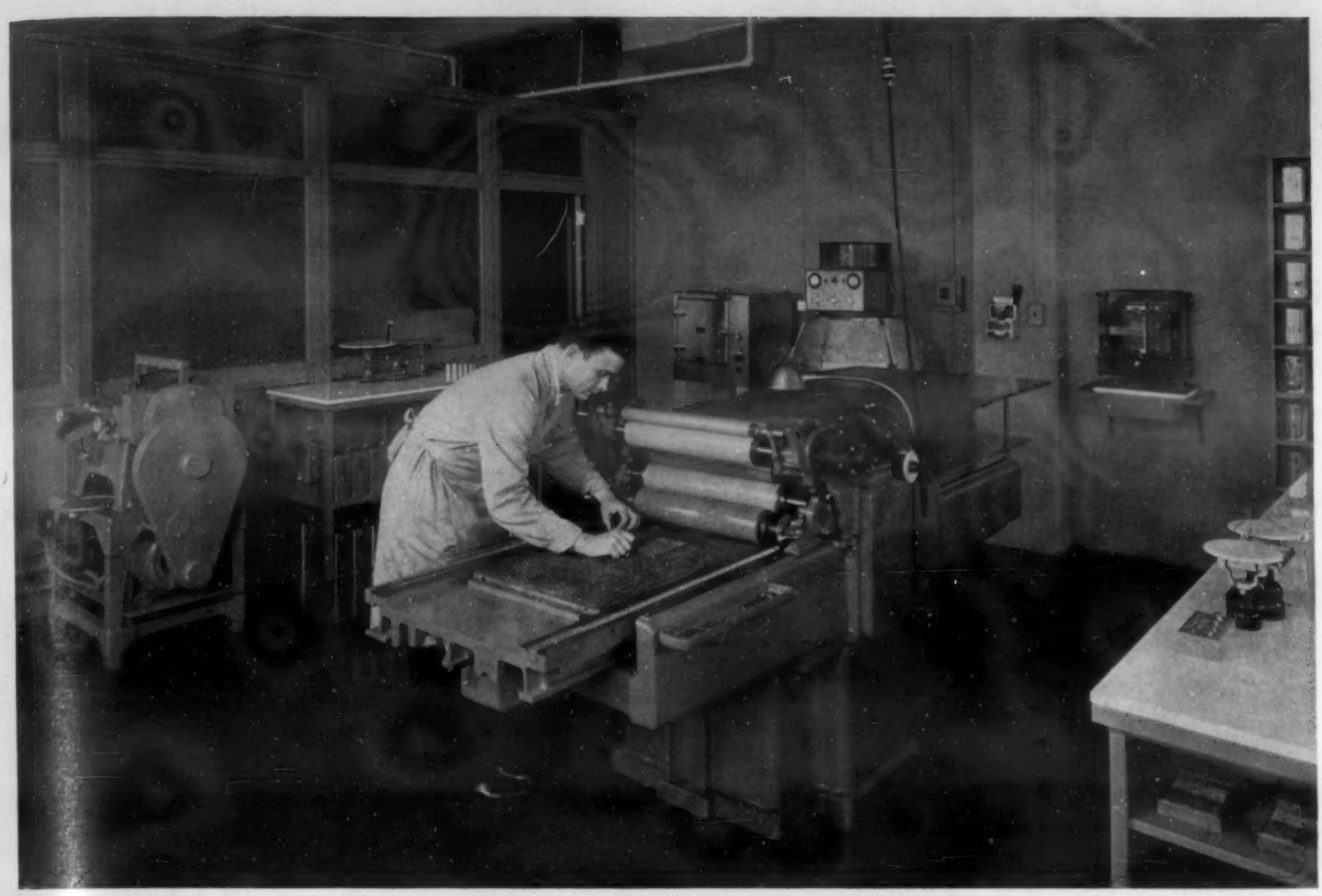
To any one accustomed to the accuracy involved in certain machine parts, say 0.00001 in. in certain bearings, and to the production of interchangeable parts in automobiles, the order of accuracy involved in proper type height is relatively coarse. Nevertheless when the softness of paper, the large size of the plates and cylinders, and the relatively light printing pressure used (about 300-400 lb. per sq. in.) are considered, the job of obtaining good uniform printing is by no means an easy one.

Finishing Electrotypes

One aspect of the precision problem is exemplified in the finishing of electrotypes. As has been stated this is one of the most expensive operations in the making of electrotypes. A certain amount of finishing is made necessary because of warpages, etc., which occur in the making of electrotypes. However, a large proportion of the finishing costs arises from imperfections in the original typeform and there would be a considerable saving in cost if the engraver and compositor took sufficient precautions to supply perfect originals and typeforms. The greater use of precision gages and precision proof presses and other precision instruments and machines that will reduce the amount of finishing is being promoted.

The extent to which some of the type manufacturers are striving to supply accurate type has been described recently by Louis[15]. He stated that the type as it comes out of the casting unit is subjected to a triple check inspection system. Gages used by each operator check the body dimensions of the type to an accuracy of plus or minus 0.0002 in. For

Press Correction by Use of Test Blocks. These blocks of hardened steel are accurately ground and lapped to type height (0.9182 in.) with relief printing lines milled in the surface. They are used at infrequent intervals to check accuracy of impression, especially on old cylinder presses, in order to correct defects in the press itself. (Courtesy: Hacker Mfg. Co.)



A Test Press for Plate Inspection before Final Printing. (Courtesy: Hacker Mfg. Co.)

6-point type, for example, the total body measurement of 24 characters, rather than single characters are checked in a gage, a method that obviously multiplies inaccuracies and insures high precision of measurement. Type height must be 0.9182 in. plus or minus 0.0005 in. as measured by a specially designed gage.

Of course, the type cannot be accurate unless the matrices and molds from which the type are cast are accurate. This offers a serious maintenance problem. There are also interesting metallurgical problems in choosing metals for matrix and mold which will stand up. Molds are usually made of nickel alloy steel, and matrices of a nickel-copper alloy. One of the type manufacturers advocates using paper cut to the proper size under the plate or overlays in the impression cylinder. This makeready or preparation of type for printing is frequently time consuming, taking as much as 10 hrs., or more on a large press. (There is no time for elaborate makeready in newspaper printing. For this reason soft packing is used and with the relatively thin and soft paper used, satisfactory printing at high speed is obtained with practically no makeready.) It cuts seriously into the working time and is consequently very costly.

The producers of precision plates and presses claim that a precision plate on a precision press will require practically no makeready, hence will save a great deal on printing costs. The interest of the metallurgist, already well accustomed to fine measurements of metals, will help encourage the idea of automatic precision methods in the printing industry.

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[14] B. H. McGar. "Sheet Brass for Photo Engraving and Etching." Graphic Arts Technical Conference, Washington, D. C., May 1936.

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Metallurgical and Commerce News

BY THE EDITORS

Russia's Steel Industry

At the luncheon of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers during the annual meeting this year, a prominent metallurgist connected with a leading American steel producer, in briefly recounting some of the impressions of a recent European trip, stated that, at the rate of development of the Russian industry as observed by him, that country's production of pig iron and steel would soon exceed that of Germany and Great Britain.

Official data give emphasis to this statement. In the annual review issues of the two leading iron and steel trade papers there are published tables of the world output of pig iron and steel. According to these authorities the record of Russia is approximately as follows in thousands of gross tons:

	Pig Iron	Steel
1936	14,000*	16,000*
1935	12,410	12,320
1929	4,253	4,828
1913	4,149	4,365

* Estimated.

This is an impressive record. Thus in 1936 the estimated pig iron output of 14,000,000 tons far exceeds the records in 1929 and 1913 and compares with about 15,300,000 tons for Germany and 7,710,000 tons for Great Britain. In steel the figures are nearly as striking. The Russian production of an estimated total of 16,000,000 tons is far ahead of earlier records as well as a substantial increase over 1935. It also is not far from the German total of 19,300,000 tons for 1936 and exceeds the British of 11,700,000 tons. Previous to 1931 Russia was less than either the British or German figures.

The Russian steel industry is developing very rapidly—not only in total output but in metallurgical progress and achievement. In this development American metallurgical engineers have played no insignificant role. With the experience and momentum already gained and with boundless resources at hand, the fulfillment of the prediction referred to will not long be delayed and Russia may be second only to the United States and displace Germany.

Trends in Actual Steel Exports

A critical analysis of our steel export data reveals an interesting fact—the totals by no means indicate actual sales abroad of finished and other important manufactured steel products. The total exports of pig iron, ferroalloys, rolled and finished steel, and castings are obtained by subtracting from the total export figures, as given officially, the amount of scrap exported. The data thus compiled and handled are as follows for 1936 and for the five previous years in gross tons:

Year	Total Exports	Scrap Exports	Actual Exports	Tons per Month
1931	968,992	136,125	862,867	71,900
1932	594,650	227,522	367,128	30,600
1933	1,341,137	773,406	567,731	47,310
1934	2,832,764	1,835,554	997,210	83,100
1935	3,067,336	2,107,814*	959,522	79,960
1936	3,162,694	1,941,031*	1,221,663	101,805

* Includes tin plate scrap.

Thus the exports of all the manufactured steel and iron—or *actual steel* exports—were down to 30,600 tons per month in 1932, the bottom of the depression. The extent of the general world recovery, as judged by such exports, is reflected in the monthly exports for 1936 of 101,805 tons. The gradual recovery is also shown by the monthly data.

An idea of the lack of actual exports, as given by usual totals, is revealed by the fact that last year the 1,221,663 tons of actual steel exports is nearly 39 per cent or 38.66 per cent of that reported for that period or 3,162,694 tons.

The table also reveals the large volume of scrap exports in the last three years, reaching over 2,107,800 tons in 1935 but decreasing last year.

Alloys in Malleable Iron

Alloyed malleable iron has become an established product by several malleable foundries. The chief alloying element is molybdenum up to 0.35 per cent. In some cases about 1.00 per cent copper is associated with the molybdenum. It is claimed that, after, the usual annealing, the malleable iron alloyed with 0.35 per cent molybdenum has a higher tensile strength and yield point than ordinary malleable and that the ductility is not appreciably affected. The same is substantially true when copper is present.

One of the products now being made of molybdenum malleable iron is a wrench handle. One of these handles, properly heat treated, was put in a vise and then twisted through 360 deg. without breaking. Handles made of the same iron have been twisted 450 deg. or 1¼ turns without breaking. This is on the authority of the Climax Molybdenum Co., New York.

Pig Iron Imports Now at Highest Volume in Years

There has been a lot of talk in these New Deal days about competition of foreign pig iron with the American product. That there is basis for this agitation can be proved by an analysis of our Government statistics. This establishes the fact that the present rate of pig iron imports is not only the largest in a number of years but is nearly 30 per cent greater than in 1913 and also the largest since before the depression.

These facts are established by the following table, compiled from official data, giving imports of pig iron in gross tons per month:

Year	Tons per Month
1936	13,826
1935	10,911
1934	9,622
1933	13,220
1932	10,890
1931	7,038
1930	11,400
1929	12,300
1913	10,900

The present volume of over 13,800 tons monthly, according to the latest data available, is nearly 30 per cent more than the 10,900 tons per month in 1913. It also exceeds the 12,300 tons per month in the boom year of 1929. Another interesting fact is that the imports now are the largest by nearly 100 per cent than the low point in the depression or 7,038 tons monthly in 1931.

Of further interest in this connection is the fact that, of the 165,909 tons imported last year, 60,363 tons have come from the Netherlands, 55,527 tons from British India, 24,556 tons from Russia, and 10,671 tons from Canada.

A Symposium on Wear of Metals

AN EXTENDED ABSTRACT

by H. W. Gillett

A symposium on "Wear of Metals" was held at the Engineers' Club, Philadelphia, April 5, under the auspices of the Philadelphia District Committee of the American Society for Testing Materials. This is said to be the first organized symposium on this important subject. The papers which made up an afternoon and evening program were as follows:

"General Discussion and Considerations Involved in Wear Testing, Including the Classification of the Various Types of Wear," by H. W. Gillett, chief technical adviser, Battelle Memorial Institute, Columbus, Ohio.
"Some Important Variables Encountered in Wear Tests on Cast Iron," by D. E. Ackerman, metallurgist, Research Laboratory, International Nickel Co., Inc., Bayonne, N. J.
"Wear from the Textile Industry Viewpoint" by Albert Palmer, Crompton & Knowles Loom Works, Worcester, Mass.
"Wear of Metals from the Railroad Viewpoint" by L. W. Wallace, director, Equipment Research Division, Association of American Railroads, Chicago.
"Wear from the Automotive Viewpoint" by W. E. Jominy, metallurgical department, Research Laboratories Section, General Motors Corp., Detroit.
"Wear from the Power Equipment Viewpoint" by N. L. Mochel, metallurgical engineer, Westinghouse Electric & Mfg. Co., Philadelphia.

G. H. Clamer, president, Ajax Metal Co., Philadelphia, organized the symposium and was chairman of the afternoon session. Pres. A. C. Fieldner of the A. S. T. M. and chief of the technological branch of the U. S. Bureau of Mines, Washington, was chairman of the evening session.

The article which follows is an extended abstract of the papers.

DIVERSE AS ARE THE PROBLEMS concerned in various types of metallic wear, there is much similarity in the proper methods for finding out how to overcome the troubles—this was the consensus of opinion at the symposium on Wear of Metals, held in Philadelphia April 5.

Simulated Service Tests

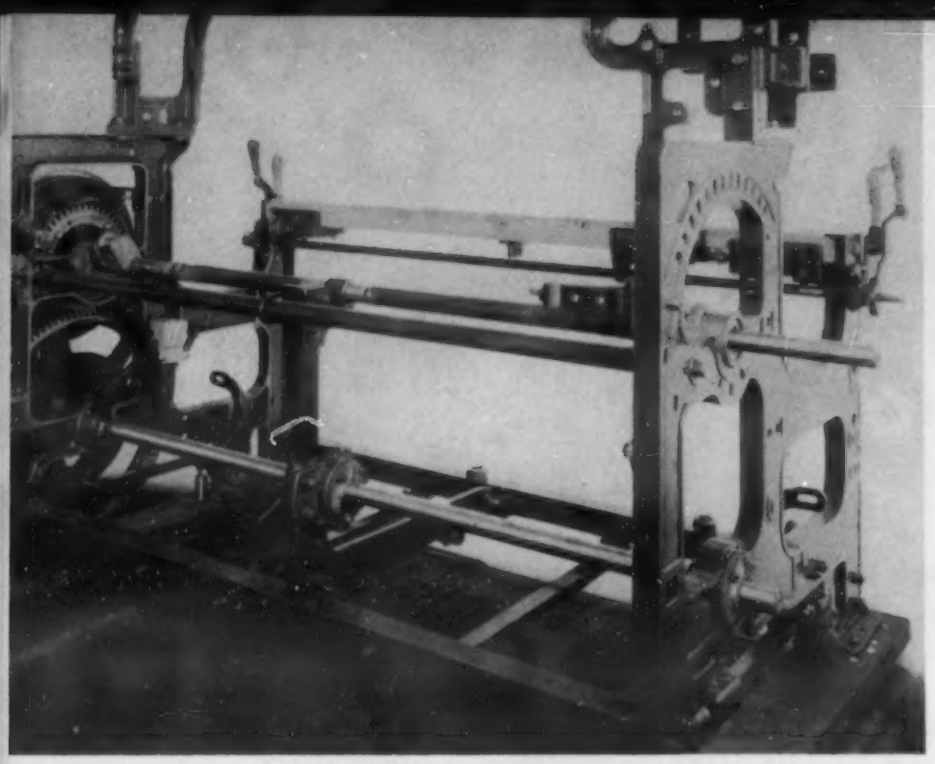
N. L. Mochel in his paper on "Wear from the Power Equipment Viewpoint," noted that some sort of laboratory test is essential in making a selection among possible wear-resistant materials for a given purpose, since the possible combinations are so extensive. Moreover, in this particular field the first guess has to be the right one, for turbines and generators are meant to run steadily without being down for repairs or replacements. In order to make the first guess right, Mochel's practice is to set up in the laboratory the particular section of the actual machine in question and run it under simulated service conditions.

Such equipment allowed the selection of a Stellite containing about 55 per cent Co, 30 per cent Cr, and 5 per cent W, as a shield for turbine blades. Besides being wear resistant against the erosion of wet steam, the material has to be capable of being formed into strips and silver soldered to the blades. The good wear resistance would not necessarily be predicted by a knowledge of its other properties, especially since it is not extraordinarily hard, and it took actual test to show its superiority.

Sealing strips used in a turbine to make a close-fitting, labyrinth type of seal must be capable of being rolled very thin and resist corrosion. Beside some other mechanical requirements, they must have the unusual one of wearing very quickly, when by any chance due to expansion in service, they actually touch the casing. They must not seize and gall the casing nor hold their contact long enough to cause local heating. The unusual requirement of very rapid wear was met by low carbon 13 per cent Cr, 0.50 per cent Mo steel, and this, too, was selected by simulated service tests in the laboratory.

Valve seats, valve stems and bushings for high temperature steam are likewise selected by simulated service tests and, for various conditions of service, Stellite, various chromium steels, age hardened K-Monel, and, where corrosion is not a factor, nitrided steels were thus selected.

In generator brushes and collector rings wear is great when they are surrounded by air or oxygen, and small when by hydrogen or CO_2. The effect of the atmosphere is so great that hydrogen cooled generators show superiority



A Modern Silk Loom Frame as It Leaves the Assembly Fixture. The machined loomsides and machined structural steel lengthwise members make a rigid assembly which is perfectly lined and squared. The shafting, though closely fitted, turns freely because the bearings are in perfect alignment—something that was not possible in the old machinery where cast iron lengthwise members were fitted by hand to rough loomsides. (From the paper by A. Palmer.)

not only in efficiency but also in wear. This was likewise shown by simulated service laboratory tests.

Cast Iron and Wear

The effect of the atmosphere on wear was brought out also by D. E. Ackerman, who discussed variables encountered in wear tests on cast iron. Amsler wear tests of "Nihard" and of ordinary chilled iron, each tested against itself, were handicapped by the development of an oxidized surface when the tests were run in air. Since this does not occur in the types of service to which chilled iron is usually subjected, the tests obviously did not have applicability and it was necessary to resort to an atmosphere of purified nitrogen. In this the Nihard showed better wear resistance than did plain chilled iron.

Since the tests were not made to duplicate service conditions, but were merely run with the material against iself, this fact of better behavior did not mean much more than the already known facts that Nihard was harder and tougher, so after these tests its proponents were emboldened to put Nihard into service, and the Amsler testing program was suspended as not throwing much light on the probable types of service. The conclusion was reached that it is "unlikely that a testing machine satisfactory for general-purpose use can be devised."

Wear in Textile Machinery

The paper by A. Palmer on wear in the textile industry recounted successful attempts to reduce wear by mechanical means, such as using bearing clearances like those of the automotive industry rather than that of a buggy wheel, and by designing for rigidity, or for resilience, depending on the type of service. The effect of the humid environment of a textile mill was brought out. Main emphasis was put on the application of commonsense principles of mechanical engineering, such as making it easy to lubricate, and providing for withdrawal of used oil or grease so that grit picked up in use would be removed from the bearing.

Mochel gave a similar example of the mechanical engineering method of attack in reference to a valve which had previously been designed so that a hot, and hence enlarged, stem had to be moved through a bushing when the valve was adjusted. By shifting things around so the cold stem went through the bushing, galling was decreased.

Wear in the Automotive Industry

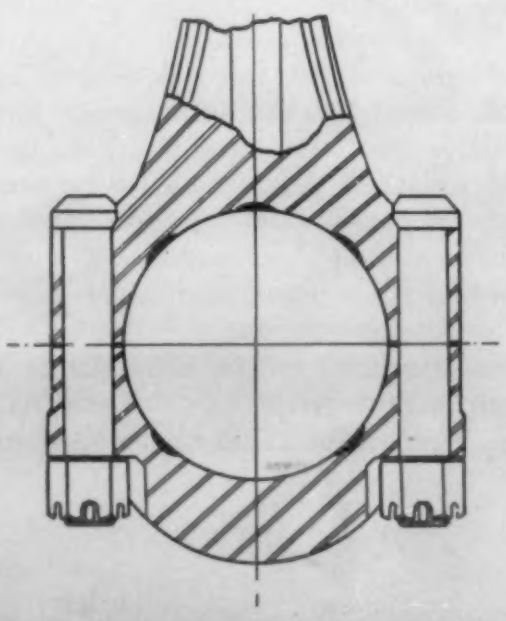
The difficulties of getting reproducible results in wear testing, and of insuring that they rate materials in the same order as that of service were brought out by W. E. Jominy in his discussion of wear from the automotive viewpoint. In working out a brake shoe type of test for study of piston ring wear, it was found advisable to apply the load slowly and, instead of running with constant load, to use a dynamometer type of control which adjusts the load to constant friction; if the surface gets rougher, the load is decreased so that friction is held constant. Otherwise close duplication of tests was not readily obtainable. In a further development of the wear test outfit, both the co-acting parts are to have their weight losses determined. In such tests cast irons with coarse graphite had better wear resistance than those with fine graphite, just as is found in service. High phosphorus was also indicated as useful.

That wear tests rather than specific property tests are what is needed is brought out by the poor performance in wear tests of hard tool steel though, from specific property tests, one without knowledge of its behavior as a piston ring would expect it to show up well.

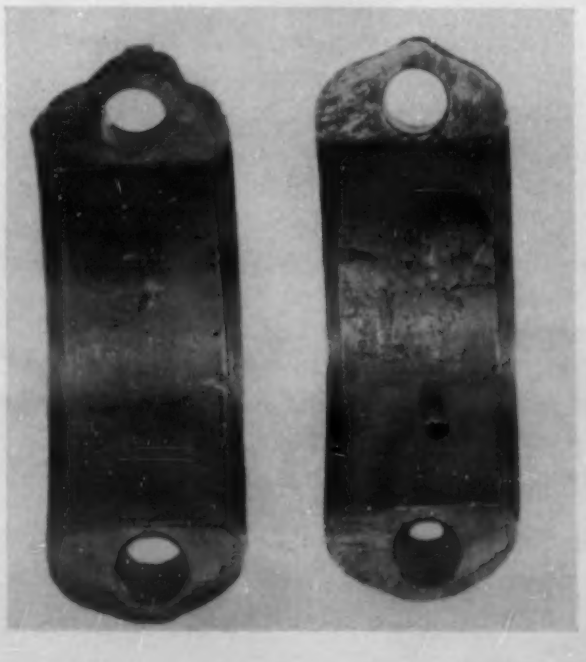
The influence of corrosion and of the atmosphere upon wear was emphasized by Jominy. He seconded Mochel in placing emphasis on the need for laboratory testing aimed to give rapid results, stating that the General Motors piston ring wear testing program, carried out in a single cylinder engine, would take 100 years to complete.

Definitions of "Wear"

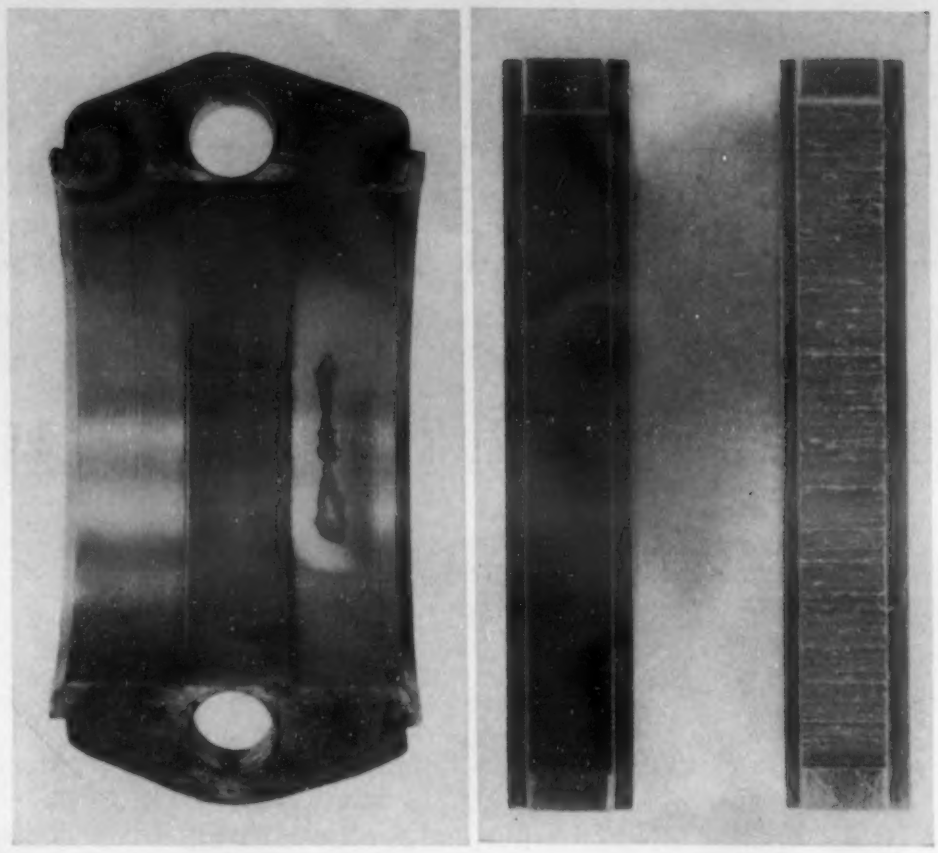
Fatigue failure in bearings and in gears, with pitting and scoring of the latter, was cited as analogous to wear, but Jominy's nomenclature is to use the word "wear" only for



Point of Flexure in Connecting Rod Bearings. High temperature weakens the Babbitt and the higher load produces an increase in flexure, causing a tendency for the bearing to fail at the five points shown—a type of failure that is often incorrectly called "poor bond.". (From the paper by Jominy.)



A Connecting Rod Bearing Which Has Failed from Fatigue. The lefthand half is the rod half of the bearing and the right hand half is the cap itself. (From the paper by Jominy.)



A Babbitt (Left) Which Has Failed at the Bond. Bearings often fail at the bond, the bond being low in strength in fatigue although the bond may be perfect metallurgically. (From the paper by Jominy.)
Wear (Right) as Effected by Lubrication. To show the tremendous effect produced by the presence of a lubricant, this photograph of wear test specimens, A (left, lubricated) and B (right, not lubricated) cut from the same bar of cast iron is shown. Specimen A was run on the wear test machine by gradually increasing the load to 9 lbs. (72 lbs. per sq. in. after the specimen was run in) and then run 10 min. at this load. No lubricant was used. Specimen B was run by gradually increasing the load to 600 lbs. (4800 lbs. per sq. in. after the specimen was run in) and run 17½ hrs. at this load, using a lubricant. The rate of wear of the non-lubricated Specimen A was 260 times faster than Specimen B in spite of the fact that the load on Specimen B was more than 65 times that of on Specimen A. As may be seen, the surface of Specimen B was left smooth whereas Specimen A was scored. (From the paper by Jominy.)

slow removal of metal that leaves a bright surface (even though corrosion might be involved) and to differentiate any welding type of wear that shows pitting, galling or scoring.

On the other hand, the other commentators used broader and broader definitions of wear. H. W. Gillett, of Battelle Memorial Institute, whose paper on a general discussion of wear testing was dealt with in our last month's comparison of wear testing with corrosion testing, ("Testing Metals for Severe Service," METALS AND ALLOYS, April, 1937) defined wear broadly enough to include dimensional changes due to metal flow as well as metal removal, and admitted corrosion as a source of wear of moving parts where the corrosion product can be removed by friction and a fresh surface worn away to corrode further. Mochel took a still broader definition "impairment due to ordinary use" and argued for the adoption of a point of view broad enough and testing methods so inclusive of all variables of service that, in simulated service, all these variables are present whether the testing engineer recognizes that they are there or not.

L. W. Wallace in his paper included impact battering, heat checking, surface cracking by fatigue, corrosion, abrasion, galling, etc., in his consideration of wear, thus taking much the same point of view as did Mochel.

Wear of Journals

Dr. G. H. Clamer recalled, in discussion, work he had done over 30 years ago on relative wear of leaded bronze bearings, his laboratory tests agreeing with the results obtained in railway service by Dr. Dudley. He cited recent work by Brownsdon which disagreed with the facts Clamer and Dudley had established and which had been corroborated in the laboratory by French, as well as by many years of actual service. Brownsdon's test method does not produce worn surfaces that look like worn bearings, and H. Meyer recently criticized Brownsdon's results, stating that "the relation of a special testing machine to the practical processes involved in wear under a particular set of circumstances must be carefully analyzed before any importance can be attached to the results of such a test." Meyer gave data again agreeing with those of Clamer as to the beneficial effect of lead in bronze. He pointed out, however, that the leaded bronzes were conducive to wear on the steel shaft and Dr. Clamer points out that the problem of journal wear is of prime importance. Thus the warning by Gillett that a wear test should give information on the rate of wear of both co-acting parts and the similar point of view of Jominy is concurred in by Dr. Clamer.

From the testing point of view, all the papers stated in different words and with varying degrees of emphasis, what Wallace put as follows: "The wear problem is a continuing one. As operating conditions change, so will this problem. This is true because wear in service may not be so much a characteristic of metals as of the conditions of use. Therefore, research methods and results will have merit only in the degree to which the characteristics of use are carefully analysed and the test procedure designed to develop results in terms thereof. It is a question whether test results not obtained in terms of conditions of use are ever safe enough even for acceptance purposes."

Wear of Grinding Mill Balls

While the symposium papers related chiefly to the metal to metal type of wear, it may be noted that Ellis, at the Ontario Research Foundation, according to the Report for 1936 finds that in tests of grinding mill balls, suitability is not determinable by abrading the ball surface away by an abrasive, such as carborundum, chosen at random, since the order of excellence thus shown bears no necessary relation to the order in service. Hence Ellis concludes that the material of the ball and the material to be ground are equally important and that the only way to select a ball is by tests that use the actual ore to be milled.

If the papers of this symposium are read by those who want to get information on wear resistance, they should go a long ways toward checking those experimenters who unthinkingly try to appraise wear by any old method of producing abrasion rather than by simulating actual service.

A NEW METHOD FOR STUDYING

Cavitation Erosion of Metals

by Walter C. Schumb, H. Peters and Lowell H. Milligan

Joint Contribution from the Research Laboratory of Inorganic Chemistry, No. 57, and the Department of Mechanical Engineering, Massachusetts Institute of Technology.

THE EROSION OF SHIP PROPELLER blades, of pump impellers, and of hydraulic turbines is a type of failure of metallurgical materials that has not been exhaustively studied. The roughening of the metal surface has somewhat the appearance of a pitting type of corrosion, but corrosion products may be substantially absent. This form of attack is ascribable to cavitation in the liquid medium, and is particularly likely to occur in modern high-speed hydraulic machinery of the rotary type.

When the relative motion between the liquid and a machine part in contact with the liquid is sufficiently rapid, the pressure head may be locally reduced to the boiling point of the liquid at that reduced pressure, i.e., local "vacuum distillation" occurs, and the cavity formed in the liquid is filled with vapor. For example, a propeller may be considered to move so fast that the water does not have time to close in on it to maintain contact, and voids or cavities tend to be produced. Then an instant later, or at points further downstream in a flowing liquid, the pressure jumps from the vapor pressure to higher pressures with instantaneous condensation of the vapor and resulting high-speed liquid impact.

Not only does cavitation produce a direct loss of energy, but its erosive effect roughens the metal surfaces involved and increases the friction, thus producing a further energy loss as well as eventual destruction of the equipment. Hydraulic engineers are therefore anxious to avoid cavitation. The mechanical design of the system, the operating conditions, the physico-chemical properties of the liquid, all need consideration. If cavitation has not been avoided, alloys best adapted to resist its destructive effects should be chosen as materials of construction.

However, the most disturbing fact is the extended and rapid erosion and corrosion of the parts where the cavitation occurs. A sponge-like appearance of the metal surface is produced. In some installations of high-speed turbines and pumps, replacements of casings and runners have been necessary after only a short time, due to the excessive cavitation damage. Many units now in operation require costly maintenance and repair. Parts of injector pumps on steam locomotives require replacement after only 4,000 to 15,000 running miles, depending on the design and the material used.

Experimental investigation of the cavitation phenomenon is still in its early stages. For many engineering problems the question is reduced to finding means of avoiding cavitation altogether by suitable designs. This is usually done by testing models of the apparatus to determine the conditions at which cavitation is initiated. Very often, however, operating conditions only slightly removed from cavitation are desirable to obtain high speed and high efficiency. Slight operating changes will then produce cavitation, and it remains a question of finding materials that will withstand the cavitation effect. In certain appliances, as for instance injector tubes, cavitation cannot be avoided and highly resistant materials should always be employed.

Cavitation can be produced under more or less controlled conditions in a large-scale hydraulic laboratory. The equipment in the hydraulic laboratory at Massachusetts Institute of Technology contains more than 5 tons of water, and erosive effects upon metals are produced with runs of 100 hrs. or more. Work with this unit has shown[1] that increasing amounts of air dissolved in the water decrease the rate of damage by cavitation erosion, but the use of such large units for a comprehensive study of the properties of liquids and solutions relating to cavitation, and of the resistance of metals and alloys to its attack, is cumbersome and unsatisfactory. An accelerated method of study on a smaller scale is much to be desired, for even though the smaller size experiments may not introduce all variables in exactly the proportion occurring in practice, highly useful indications, at least, are to be expected by more simple production of cavitation phenomena.

The periodic nature of cavitation as occurring in hydraulic practice is well established. By employing other experimental methods, it is possible to vibrate a solid in contact with a stationary liquid with sufficient intensity to result in cavitation. Equipment for generating such vibrations of sonic or ultrasonic frequencies was built in the Eastman Laboratories at Massachusetts Institute of Technology with the original purpose of studying the influence of these vibrations upon chemical reactions. This apparatus has proved to be particularly suitable for producing cavitation under controlled conditions, (preliminary statement of its use for this purpose is given by J. C. Hunsaker, *Trans.*, A.S.M.E., Vol. 57, 1935, page 423) and experimentation was therefore directed toward its use for studying cavitation erosion of metals.

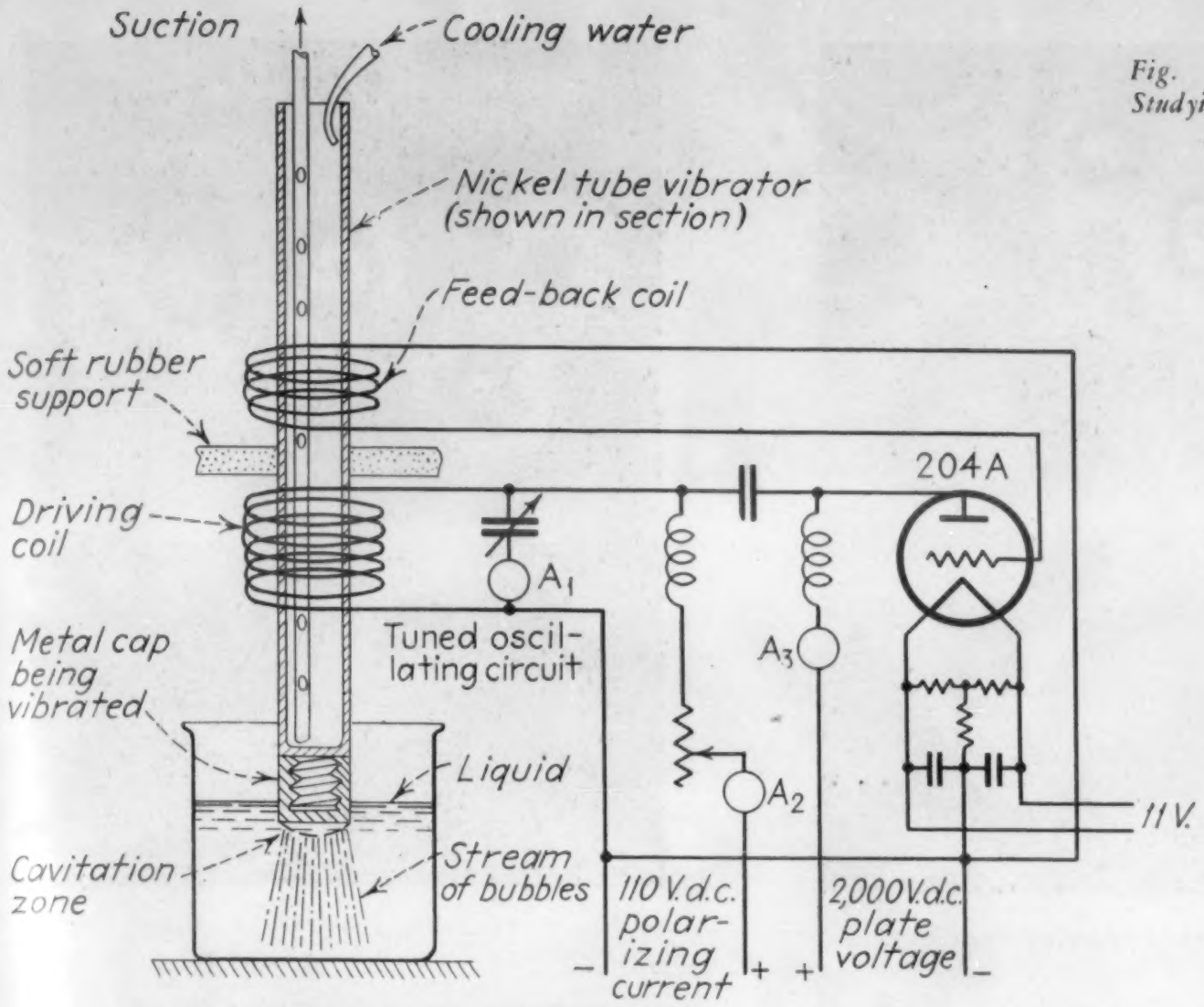


Fig. 1. Apparatus for Studying Cavitation Erosion of Metals.

The Equipment Used

The apparatus employed is based on that of Gaines[2] but differs from his arrangement in a number of ways. A schematic diagram is shown in Fig. 1.

Intense vibrations of frequency approximately 9000 cycles per sec. are generated by longitudinal vibration of a vertical nickel tube, the lower end of which is closed with a cap that is immersed in the liquid. Cavitation occurs in the liquid directly beneath the cap. The tube is driven at its natural vibration frequency by an oscillating electric current tuned to the proper frequency, and vibrates because of the magnetostrictive properties of nickel. The ends of the tube move up and down like pistons in opposite phase, whereas the center of the tube constitutes a node and undergoes only alternate extension and compression.

The nickel tube is hard-drawn (regular stock tubing from the International Nickel Co.), 12 in. long by 5/8 in. O.D. and 0.028 in. wall thickness. The lower end has a nickel or brass plug silver-soldered into it, and the projecting portion is threaded so that removable caps of various metals can be screwed to it. For attachment or removal these caps are gripped in a split brass block, that was drilled with a hole before splitting, and is faced with leather. With this arrangement held in a vise, the caps can be attached tightly, but without marring or change of weight.

It is essential that the plug closing the lower end of the tube be well soldered in place, and that the removable metal cap be fastened in place very tightly, as any looseness whatever reduces the amplitude of the vibration. It sometimes has been found desirable to smooth the upper edge of the caps by hand-lapping with a loose abrasive in order to obtain uniform bearing contact between plug and cap around the outer edge. Good vibration and cavitation results were obtained when the total added weight of the metal plug and cap was about 25 grams, but too much weight prevented maximum response.

In some work with solutions corrosive to metals, a cap of inert erosion-resistant material was made of molded boron carbide ("Norbide") supplied by the Norton Co. In this case the cap was not removable, but consisted of a solid plug, copper plated on its upper end and soft-soldered directly into the nickel tube. It was used for a number of hours of vibration before marked dulling of the polished surface was apparent.

Considerable heat is generated in the vibrating tube, and this has to be dissipated or the vibration ceases. Cooling water at constant head is delivered at the top of the nickel tube, and withdrawn at the bottom, through the glass tubes shown. Uniform and substantially complete removal of the water must be effected in order not to damp the vibration or alter the frequency of the tube. This is accomplished by withdrawing some air together with the water, and then separating the air from the water in an inverted suction flask and allowing the water to drain out to the sink through a water column equal to the air-line suction applied. The electrical coils are cooled by blowing air on them with a fan during operation.

The coils are made of asbestos-covered copper wire ("Deltabeston"). Their dimensions and characteristics are given in Table I.

Table I.—Dimensions and Characteristics of Coils.

Coil	O.D., in.	I.D., in.	Thickness, in.	Wire Gage (B&S), No.	Impedance at 1000 cy., m.h.	D.C. Resistance, ohms
Driving	3⅞	1	1½	18	24.7	3.3
Feed-back	3½	1	1⅛	22	37.5	8.28

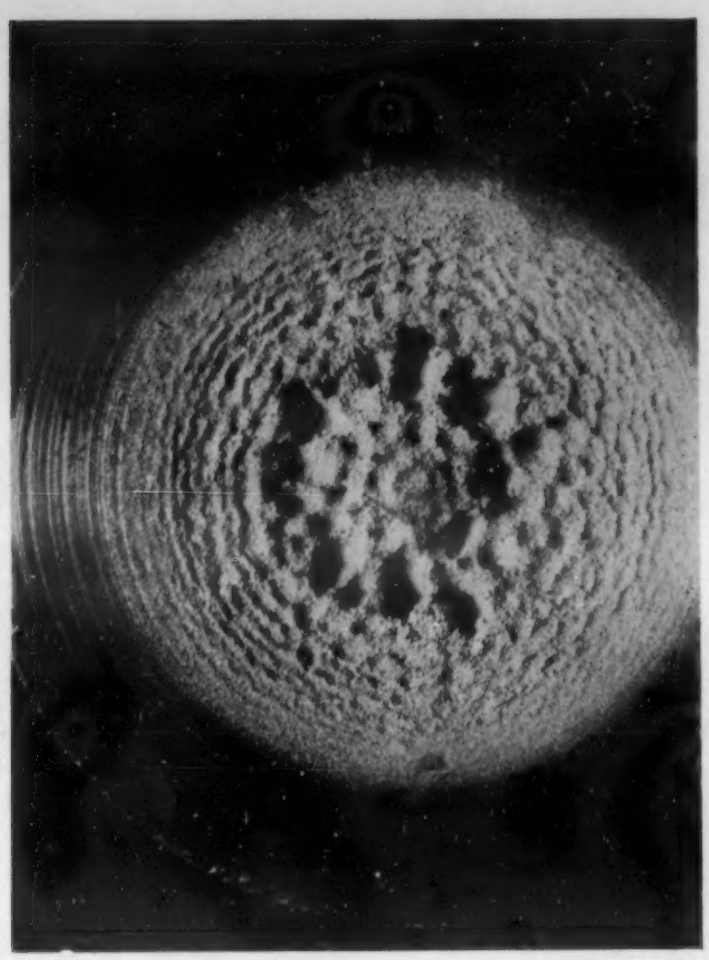


Fig. 2. Cavitation Erosion of Brass Cap.

Fig. 3. Cavitation Erosion of Cast Iron Cap.

By direct observation of the end of the nickel tube with a microscope, the maximum limits of movement were found to be about 0.10 mm. apart. The frequency determined stroboscopically was found to be about 8700 cycles per sec. The maximum acceleration was therefore approximately 15,000 times that of gravity.

Appearance During Operation

During operation of the vibration unit, a stream of fine bubbles extends downward in the liquid below the flat end of the metal cap. The liquid is in rather violent agitation, circulating downward below the cap and upward adjacent to the walls of the containing vessel. The erosion pattern

Fig. 4. Cavitation Erosion of Cold Rolled Steel Cap.

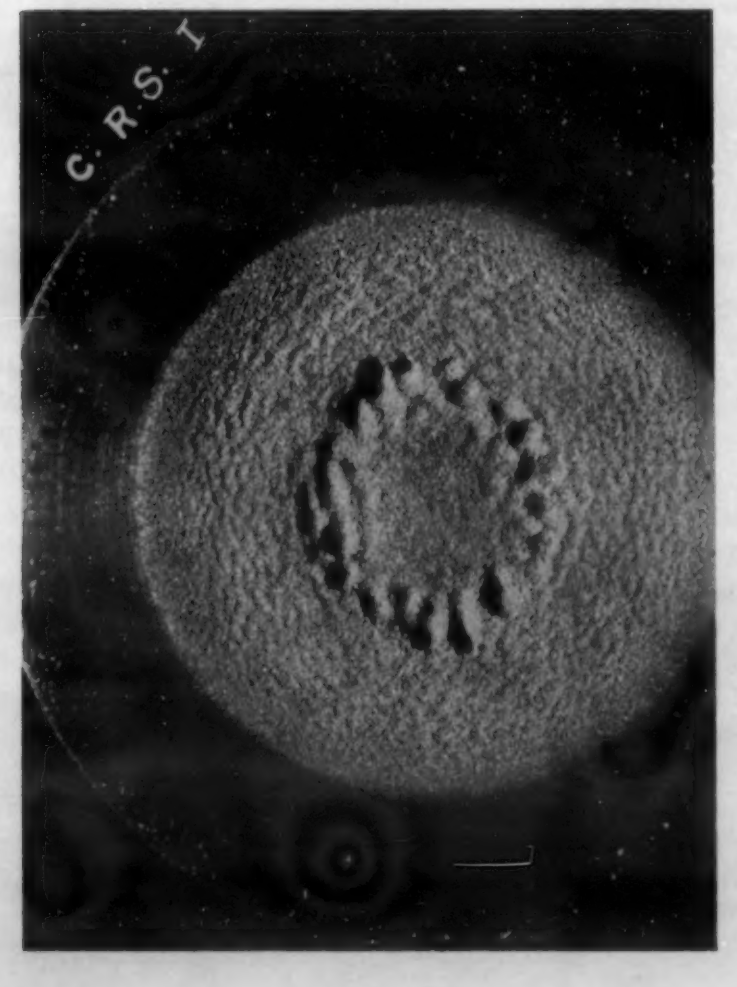
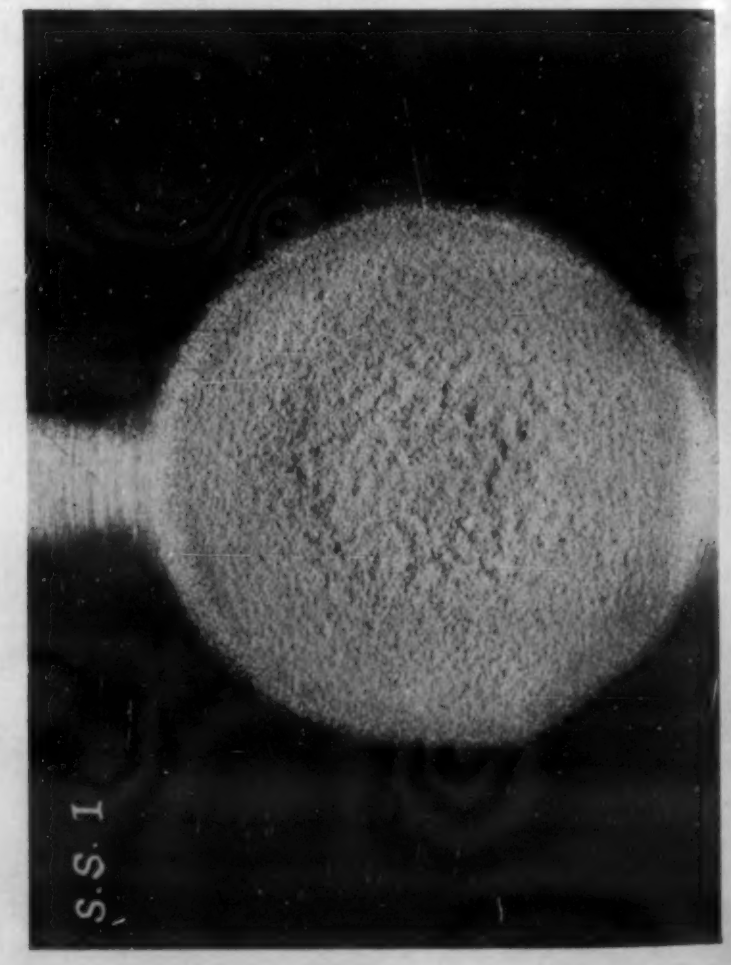
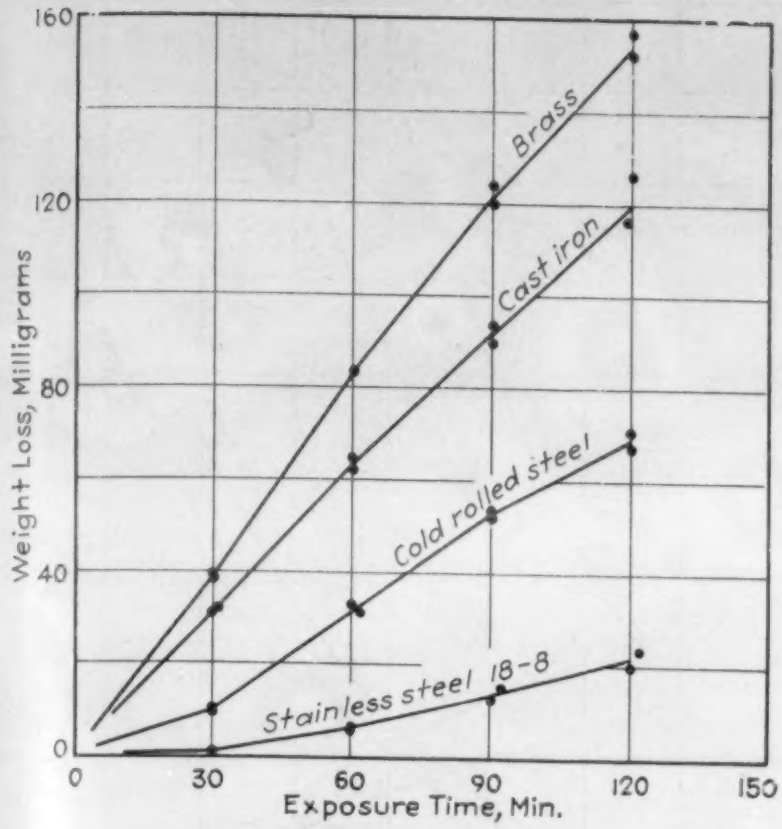
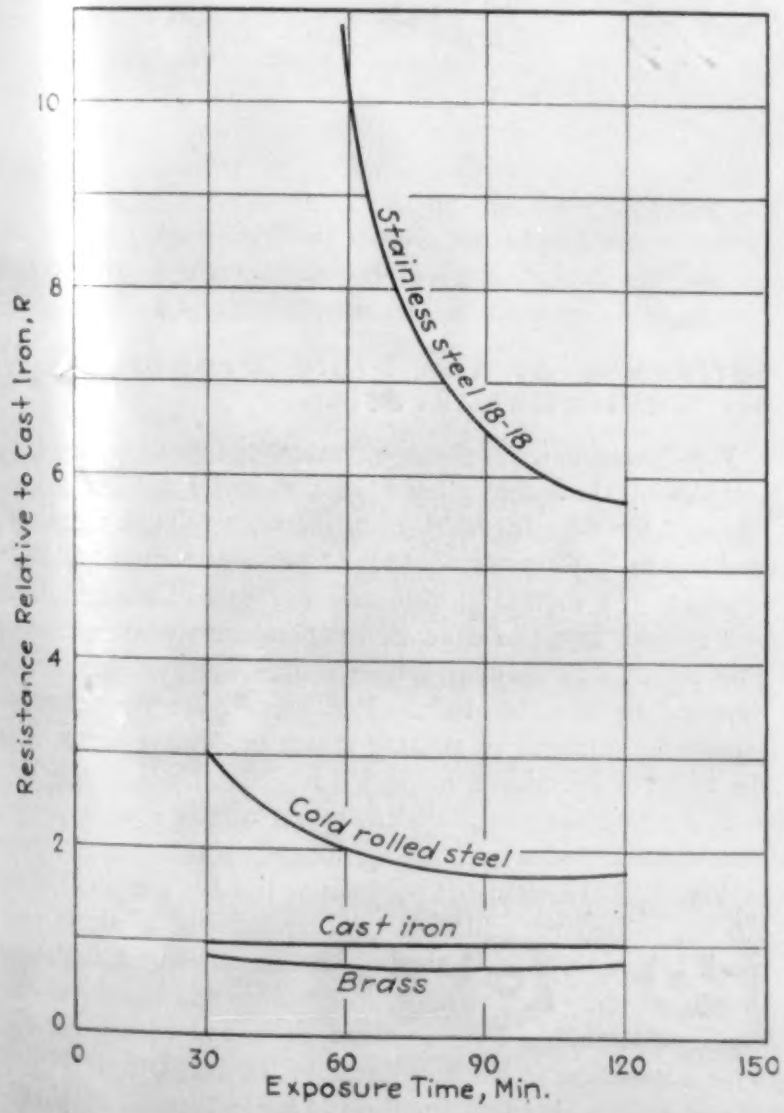


Fig. 5. Cavitation Erosion of Stainless Steel Cap.





Figs. 6A and 6B. Curves Showing Rate of Cavitation Erosion of Four Different Metals in Water at Room Temperature. Fig. 6A is the upper one.



produced on the cap has a diameter of about a centimeter. The liquid evidently flows around the edge of the cap fast enough to follow the vibratory motion near the edge without producing a cavity there. The degree of erosion increases toward the center of the cap. Figs. 2 to 5 show typical erosion patterns. The pitted areas suggest in appearance a mountainous country filled with volcanoes.

The chips produced by the cavitation erosion are like shreds of metal of very irregular shapes. They settle usually to the bottom of the vessel and usually are not fine enough in size to become colloidally dispersed. Under the microscope, chips of aluminum, copper, brass, etc., are bright and shiny, indicating little if any oxidation. There are, however, indications on some of the metal caps that a trace of oxidation took place. Those portions of the copper and brass caps that had been in the water but were outside the erosion zone were covered with slightly dark, slightly iridescent films. On the brass cap, just around the eroded area, was a zone that developed a beautiful red iridescent color. The cold-rolled steel cap was slightly yellowish over the eroded area. These films and colors indicate a trace of oxidation connected with the cavitation —due perhaps to the traces of hydrogen peroxide that were found to be formed in the water—but the magnitude of the oxidation effect is so minute as to be considered negligible as far as any possible influence on the erosion rate under our operating conditions is concerned.

Resistance of Metals to Cavitation Erosion

Experimental Series A: In these experiments caps of five different metals were tested by vibrating in water for several consecutive periods of exactly 5 min. each. Distilled water at room temperature was used, freshly drawn from the supply tank of the building for each vibration period. A volume of 150 cc. was contained in a glass cylinder to give a 9 cm. deep water column, and the immersion depth of the metal was approximately 1/8 in. The temperature rise in the water was 11 to 12 deg. C. above room temperature in each vibration period.

The metal caps were of different lengths depending upon the specific gravity of the metal used, with weights ranging from 7 to 14 grams each. The nickel plug that was soldered into the nickel tube weighed 13 grams, giving a total added weight of from 20 to 27 grams over that of the nickel tube itself which alone weighed in the vicinity of 95 grams.

The average results obtained for several tests (omitting the first two for each new cap which tended to be lower than the third and subsequent tests) are reported in Table II.

Table II. Average Results of Tests of Metal Caps.

Metal	Cavitation Erosion (milligrams loss in weight per 5 min. period)
Ordinary brass	10
Aluminum, commercially pure	30
Copper, commercially pure	27
Tobin bronze	7
Cold rolled steel	(0.5)*

* This value is the average of the first two tests on two different specimens, and is likely to be too low relative to the other values presented because a fresh smooth surface tends to erode less rapidly at first. The total erosion for this cold rolled steel was very slight and hence the surface had not departed much from its original smooth condition during the tests that are averaged.

Experimental Series B: In the next series of experiments, the metals tested were brass, cast iron, cold rolled steel, and 18 and 8 stainless steel. A different nickel tube from that used in Series A was employed, and the experiments were made by another operator. The experimental conditions were not exactly the same as those previously used, but they were maintained constant throughout the

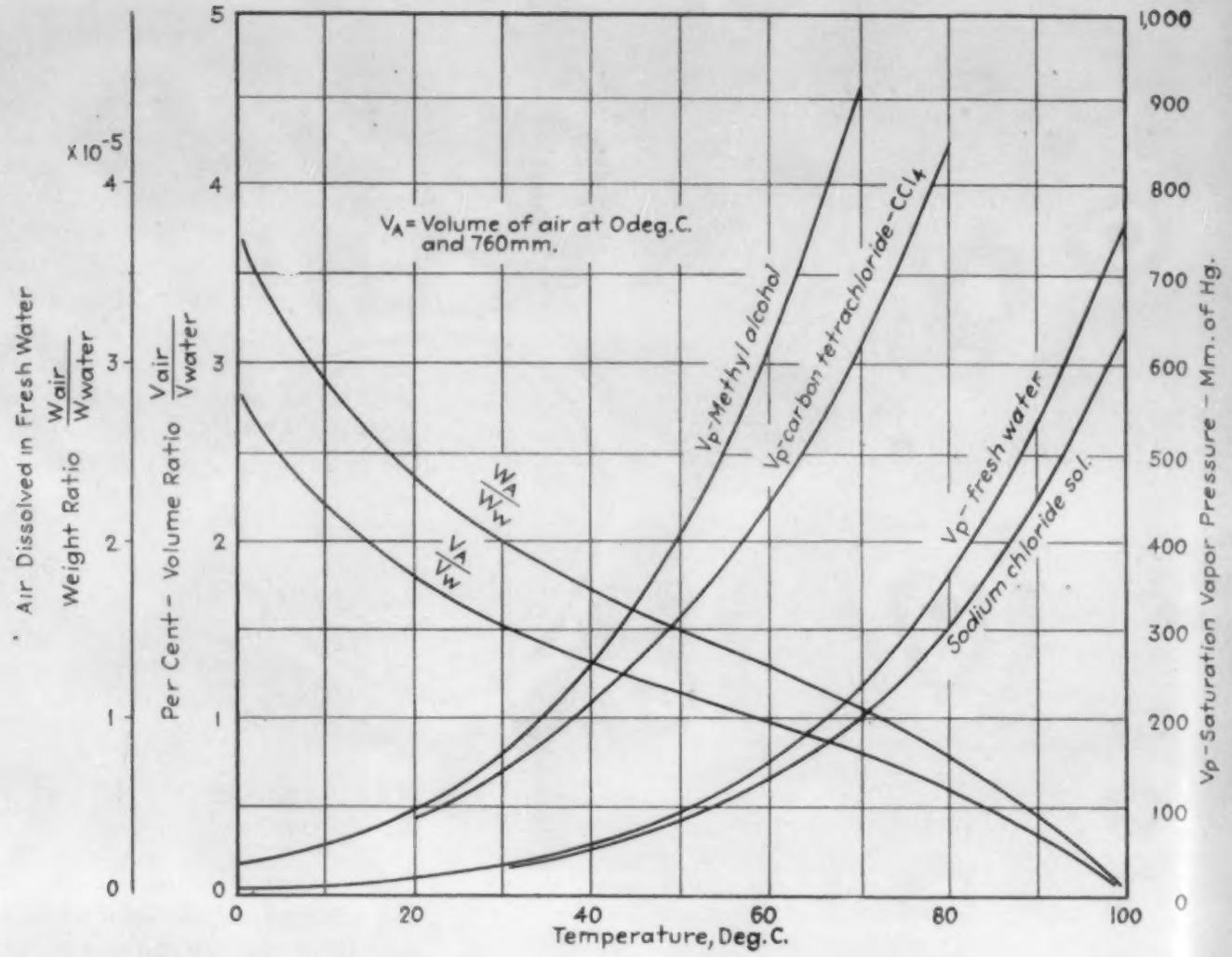


Fig. 7. Air Dissolved in Fresh Water and Saturation Vapor Pressures of Various Fluids vs. Temperature.

series. Two samples of each metal were tested in tap water at 20 deg. C. contained in a 600 cc beaker, and the depth of immersion was about 7/16 in. The testing time consisted of four 30-min. intervals.

The results, plotted in Fig. 6A show the weight loss vs. time of exposure to cavitation. The increasing slope that is particularly apparent for the steel curve is thought to be due to erosion resistance of the initially polished surfaces. After the surfaces have been pitted the erosion proceeds more rapidly.

To obtain a relative scale of resistance, the weight losses of the different materials were compared with the weight loss of cast iron for equal intervals of testing time, thus giving a number of relative resistance:

$$R_{wt.} = \frac{\text{weight loss of cast iron}}{\text{weight loss of material X}}$$

These numbers of relative resistance are plotted in Fig. 6B against the time of exposure to cavitation. The curves indicate that R_{wt} reaches an approximately constant value after a certain time of exposure. In accordance with this scale, 18 and 8 stainless steel is about 5.5 times more resistant than cast iron, cold rolled steel is 1.5 times more resistant, but brass is only 0.8 times as resistant. This order of resistance is in general agreement with observations of cavitation damage in practice.

For metals of different density a more logical scale of resistivity could be established by comparing the loss of volume, such as:

$$R_{vol.} = R_{wt.} \left(\frac{\text{density of material X}}{\text{density of cast iron}} \right)$$

This is especially apparent if one compares the damage done on the 51 S T aluminum alloy sample used for later tests. This, after a 30-min. test in water at 20 deg. C., lost 45 mg. in weight, resulting in:

$$R_{wt.} = \frac{\text{weight cast iron lost}}{\text{weight alloy lost}} = \frac{31}{45} = 0.69;$$

$$\text{and } R_{vol} = 0.69 \frac{2.7}{7.2} = 0.26$$

Photomicrographs are shown in Figs. 2 to 5 which illustrate the cavitation damage to caps made of brass, cast iron, cold rolled steel and stainless steel.

Influence of the Fluid Properties on Cavitation Erosion

For investigation of the effect of the fluid properties, samples of aluminum alloy 51 S T of the same stock were vibrated for 40 min. in 10-min. intervals. Tests were carried out in (1) tap water, (2) 20 per cent sodium chloride solution, (3) methyl alcohol and (4) carbon tetrachloride, and in each case the effect of temperature was determined. The liquid was held in a thin walled iron container surrounded by a water bath. Different operating temperatures were attained by passing steam or cooling water into the bath, or by adding ice to it.

The properties of the liquids tested vary in a wide range. The vapor pressures plotted against temperature are shown in Fig. 7. The densities vary from 0.8 for the alcohol to 1.6 for carbon tetrachloride. The solubility of air is very much higher in methyl alcohol and in carbon tetrachloride than in water. Larger range in density and viscosity of the liquids chosen has been avoided to safeguard against too wide a variation in the amplitude of the oscillation.

The results obtained for the cavitation erosion of aluminum alloy 51 S T in the four liquids at the different temperatures tested are given in Figs. 8 to 11. The results indicate that under the prevailing cavitation conditions a temperature of maximum weight loss exists in the vicinity of 40 to 50 deg. C. in water and in 20 per cent sodium

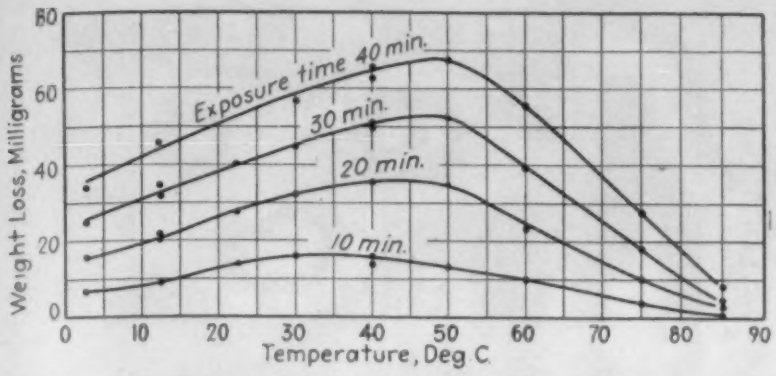


Fig. 8. Cavitation Erosion of Aluminum Alloy in Fresh Water. Weight loss vs. temperature for different times of exposure.

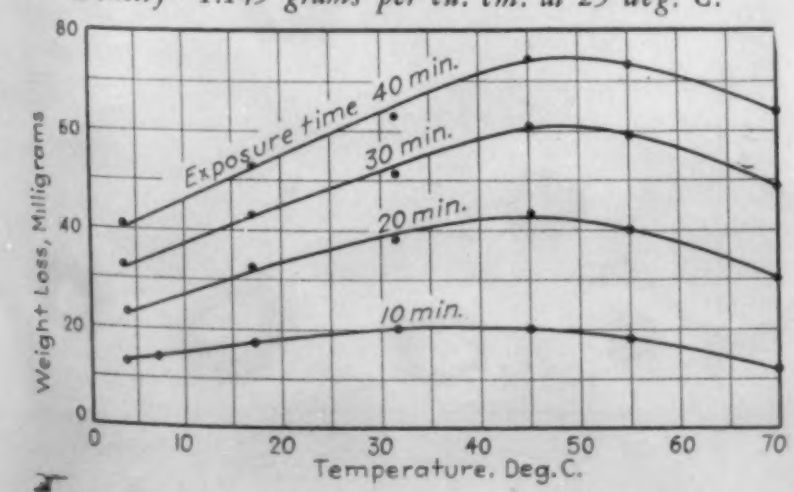
chloride solution. No maximum was found in methyl alcohol over the temperature range studied, but in carbon tetrachloride a maximum was found around 25 to 30 deg. C., and a minimum was also indicated around 18 deg. C. Approximate relative rates of cavitation erosion at room temperature of aluminum alloy 51 S T in the different liquids, in comparison to the rate in water taken as unity, were as follows:

Water	1.0
20 per cent NaCl solution	1.15
Methyl alcohol	0.10
Carbon tetrachloride	0.10

It is obvious from the above detailed data that the severity of cavitation damage depends on more than one property of the liquid. Properties that possibly have an effect might be listed as follows: Density, vapor pressure, solubility of gases, surface tension, viscosity, thermal properties, compressibility, etc.

The few data available do not permit the drawing of definite conclusions as to the relative importance of the above variables. The influence of the density cannot be discovered. The tests in methyl alcohol and carbon tetrachloride show a weight loss of the same order of magnitude in spite of the fact that the densities vary by a factor 2. The effect of the vapor pressure, or better, of the ratio for the different liquids of the vapor pressure p_v to the external pressure p (in this case atmospheric) is apparent. A decrease of damage with an increased ratio occurs after the temperature of maximum weight loss is exceeded. A comparison of weight loss on the basis of equal vapor pressure, however, shows that the pressure ratio $\left(\frac{p_v}{p}\right)$ itself is not of major importance to the severity of cavitation damage. For instance, at a vapor pressure of 190 mm. Hg or $\left(\frac{p_v}{p}\right) = 0.25$ the weight losses after 40 min. of exposure are: In fresh water, 0.046 gm.; in sodium chloride solution, 0.065 gm.; in alcohol, 0.003 gm., and in carbon tetrachloride, 0.003 gm.

Fig. 9. Cavitation Erosion of Aluminum Alloy in Sodium Chloride Solution. Concentration—20 per cent by weight. Density—1.145 grams per cu. cm. at 25 deg. C.



Unfortunately, the influence of the vapor pressure cannot be separated from the possible effect of other properties by the above data. Other properties of the liquid besides the vapor pressure vary from liquid to liquid and with a change in temperature. Especially does the order of magnitude of solubility of gases vary, and the amount of gases dissolved in the liquid is known to affect the severity of cavitation damage. The severity decreases with increased gas content, since the dissolved gases appear to come out of solution in the cavity and then to cushion the intensity of each impact following cavity formation. Vapor of the fluid itself appears to act somewhat similarly. In methyl alcohol and carbon tetrachloride, atmospheric gases have a much greater solubility than in fresh water. This could account for the much greater weight loss in fresh water compared to the two organic liquids. Likewise, air has a lower solubility in sodium chloride solution than in fresh water and the tests in the salt solution show a little more erosion.

This conclusion of the important effect of the gas content has been further substantiated by a single test in partly deaerated methyl alcohol. The weight loss was on the order of ten times greater than for the tests in alcohol saturated with air. Measurements of the air content of the liquids under test showed that an equilibrium of air content was reached after about 10 to 20 min. of vibration. This air content was slightly below the normal content of saturation.

The effect of the amount of air dissolved could also explain the existence of a temperature of maximum weight loss. The influence of the air dissolved may counteract the effect of the vapor pressure.

From the foregoing it seems that the air content is of great importance in determining the order of magnitude of the weight loss, but the part it plays in shaping the weight-loss—temperature curves can not yet be estimated. Further extensive tests in which the several properties are varied one at a time are desirable. Experiments are in progress that, we hope, will contribute to the solution of the problem.

NOTE: Extensive tests on a large number of materials have been carried out for the U. S. Engineers Office, Eastport, Me., in connection with the Passamaquoddy power project.

Furthermore, in the application of the foregoing considerations to a practical case of cavitation erosion, it must be borne in mind that the tests herein described deal with accelerated erosion, and therefore the effect of chemical *corrosion,* exerted over a considerable period of time, which in the practical case might be of serious moment, may be of negligible importance in these tests of short duration. Again, such structural changes as may take place in various metals and alloys when in service over an extended period of time, can hardly be expected to take place in the brief periods employed in our tests. Consequently, for a fair estimate of the expected extent of damage to a given metallic material, used for a particular purpose, the influence of all such effects other than cavitation must be considered.

Resistance to Cavitation Erosion vs. Sand-blast Impact Abrasion

Resistance to sand-blast impact abrasion was determined for most of the metals used in the cavitation tests. The sand-blast tests were made using No. 30 grain size of "E-1 Alundum" (crystalline alpha alumina) abrasive grain. Blasting was done in a machine designed and manufactured by the Carl Zeiss Co., Jena, Germany. For comparative purposes, data taken under the same test conditions on a sample of plate glass are included. The details of the sand-blasting method will not be repeated here since they are already available in the literature.[3] The sand-blast gives high velocity compressional impact with hard sharp-edged grains of Alundum abrasive.

Results of the sand-blast tests on the different metals compared to the average relative cavitation erosion are given in Table III.

Table III.—Results of Sand-Blast Tests on the Different Metals

Metal	Depth of Sand-Blast Penetration * (After 30 blasts with No. 30 E-1 Alundum abrasive grain at 25 lbs. air pressure on the dial gage)	Relative Cavitation Erosion
Cold rolled steel	0.36 mm.	4
Copper, commercially pure	0.37	27
18-8 Stainless steel	0.41	1
Aluminum, commercially pure	0.52	30
Tobin bronze	0.60	7
Cast iron	0.79	8
Brass	1.05	10

* Sand-blast penetrations were taken on plate glass for reference purposes under the same conditions except that a total of only 5 blasts were used, readings of the depth being made after each individual blast, as follows: 1 blast, 1.79 mm.; 2 blasts, 2.60 mm.; 3 blasts, 3.09 mm.; 4 blasts, 3.45 mm., and 5 blasts, 3.70 mm.

There appears to be little direct relationship between the sand-blast penetration values for the different metals and the relative cavitation erosion, but some of the apparent extreme discrepancies can be cleared up by a little study of the results. Aluminum and copper are very soft metals, and yet they stood up well under the particular type of sand blasting used. However, in the case of the aluminum sample, a raised rim of metal was found around the edge of the sand-blast hole, showing that the aluminum had actually flowed from under the impact area, and that its apparent sand-blast resistance was really connected with its plastic deformation. No raised rim was visible for the copper sample, but nevertheless plastic deformation would also be likely to occur readily with the soft copper.

Plastic deformation would also be expected to play a part in the cavitation erosion. Hunsaker[1] calls attention to it in connection with cavitation damage to discs of lead. The fact that under our conditions of test, more relative damage occurred to copper and aluminum by cavitation than by sand-blast may simply mean that the particular sand-blast conditions were such as to permit greater relative absorption of energy by plastic deformation than was permitted under the cavitation conditions, and not that the inherent mechanism is necessarily fundamentally different. Certainly, however, if similarity be assumed, the area of each single impingement in cavitation is much smaller, and the energy per unit of single impingement area much greater, than for the sand-blast conditions used. From this point of view, erosion by an extremely high velocity stream of water of minute cross section projected perpendicular to the metal surface, would give a closer parallel to cavitation erosion.

The sand-blast and cavitation results for cold rolled steel, Tobin bronze, cast iron, and brass line up quite well with each other. But perhaps this is due to a fortuitous combination of factors. There is nothing in these data to indicate why the 18 and 8 stainless steel is

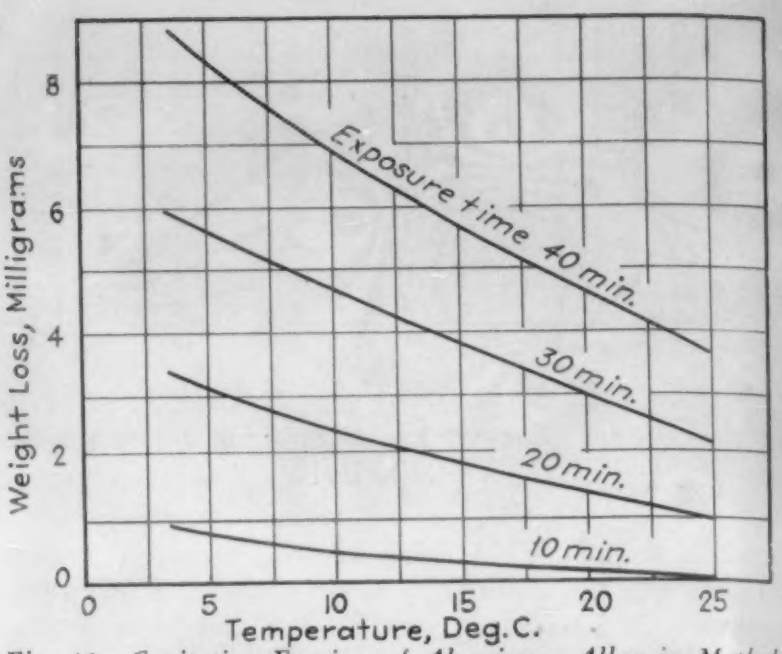


Fig. 10. Cavitation Erosion of Aluminum Alloy in Methyl Alcohol. Weight loss vs. temperature for different exposure times.

so relatively resistant to cavitation erosion compared even to cold rolled steel.

In the case of one of the copper caps having a central cavity on the inside (produced by the tip of a drill employed in making the cap), the cavitation that had occurred on the outside of the cap had caused the bottom of this cavity to fill in as if the metal were being hammered upward from below. This would be expected, and appears to be analogous to pressure effects accompanying cavitation in practical hydraulic apparatus.

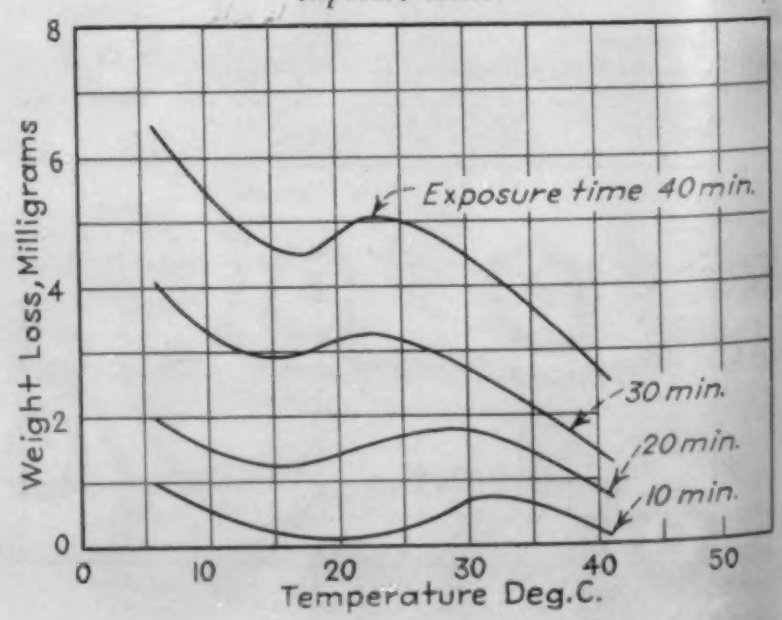
Acknowledgment

The valuable assistance of Brandon Rightmire is acknowledged in carrying out the cavitation tests of Series B on metals and of the duralumin samples in different liquids.

Thanks are expressed to the Norton Co. of Worcester, Mass., for furnishing the molded boron carbide plug ("Norbide") used on the inert erosion-resistant vibrator, and for the use of the Zeiss sand-blast impact abrasion testing machine.

[1] J. C. Hunsaker. *Mechanical Engineering*, Vol. 57, 1935, page 211.
[2] N. Gaines. *Physics*, Vol. 3, 1932, page 209.
[3] Lowell H. Milligan. *Journal*, American Ceramic Society, Vol. 19, July 1936, page 187. (Attention should be called to the fact that most of the data in this reference were taken using round-grained quartz sand as the abrasive, which does not cut so fast as the E-1 Alundum grain.)

Fig. 11. Cavitation Erosion of Aluminum Alloy in Carbon Tetrachloride. Weight loss vs. temperature for different exposure times.

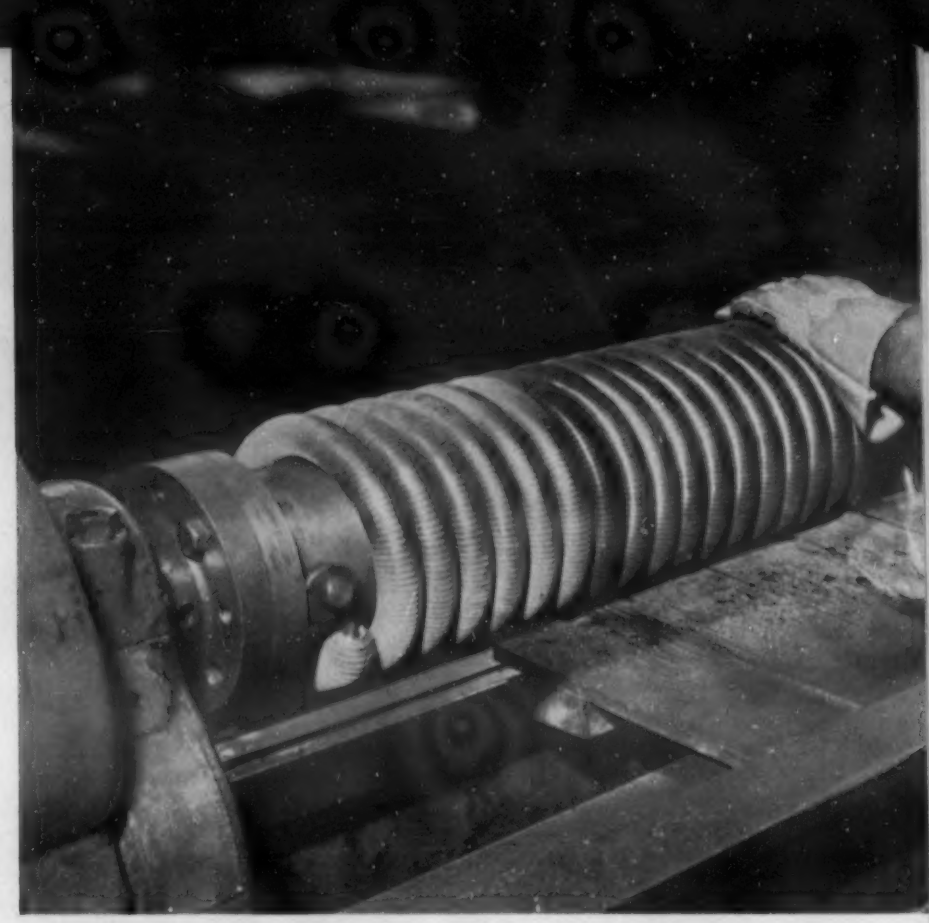


THE MANUFACTURE OF

FINNED COPPER TUBING

OF COPPER OR ALUMINUM

by Edwin F. Cone



Preparing Coils of Finned Copper Tubing

THERE ARE MANY INSTANCES in industry where intricate metal products require difficult mechanical manipulations in fabrication. In such cases production is often radically simplified by the development of a special machine. This usually results in a better product and in larger production. An excellent example of this is finned tubing of copper and aluminum.

For a number of years the Wolverine Tube Co. of Detroit, manufacturers of copper, brass and aluminum tubing, has been turning out tubing which has fins of metal of tapered thicknesses on the outside. This product is used in heat exchangers.

Until the new process, here described, was perfected, the fins of thin metal were attached to the tube in separate pieces—by casting, brazing, welding or other means. This naturally involved much labor and time. Even under the most favorable conditions the resulting product was not all that could be desired. For example, where high temperatures are involved and, where vibration has to be withstood, tubes with fins attached by the older methods are not in all respects satisfactory.

A Special Machine Developed

In order to produce a product not subject to the objections mentioned above, the Wolverine Tube Co. set about to develop a machine which would turn out a finned tube made from solid metal—a tube in which the fins would not be attached by any mechanical means. After several years of experiment and research, a machine was perfected which passes a tube of metal between a set of rolls which so work the metal that a one piece finned tube emerges.

As indicated by one of the illustrations, the two rolls are so constructed that the metal tubing, as it passes through, meets successively a series of flutings in the rolls, varying progressively from a V shape to a slot. The metal is thus gradually extruded by the rolls until fins of definite thickness and spacing result. By far the largest production is copper finned tubing though considerable aluminum finned tubing is made.

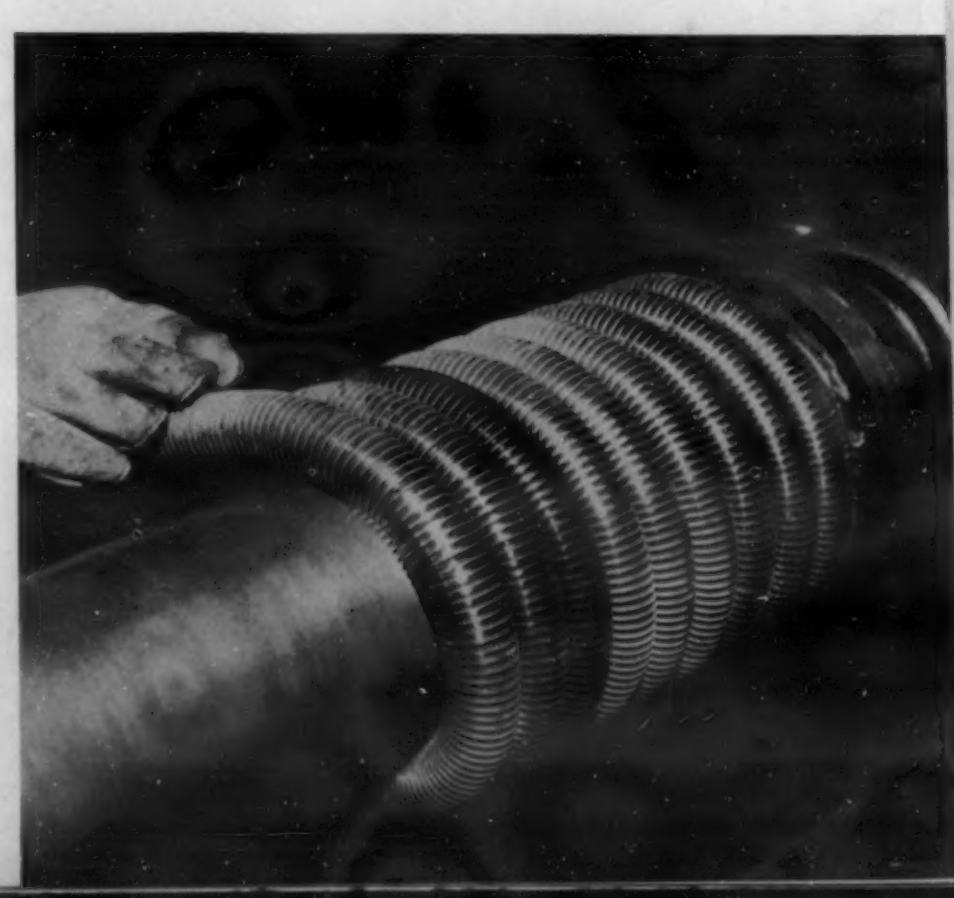
The rolls of the finning machine are made of an unalloyed, 1 per cent carbon steel, heat-treated to a hardness of Rockwell C 40 to 45. Rolls of this composition have been found to be equally as satisfactory as any alloy steel rolls.

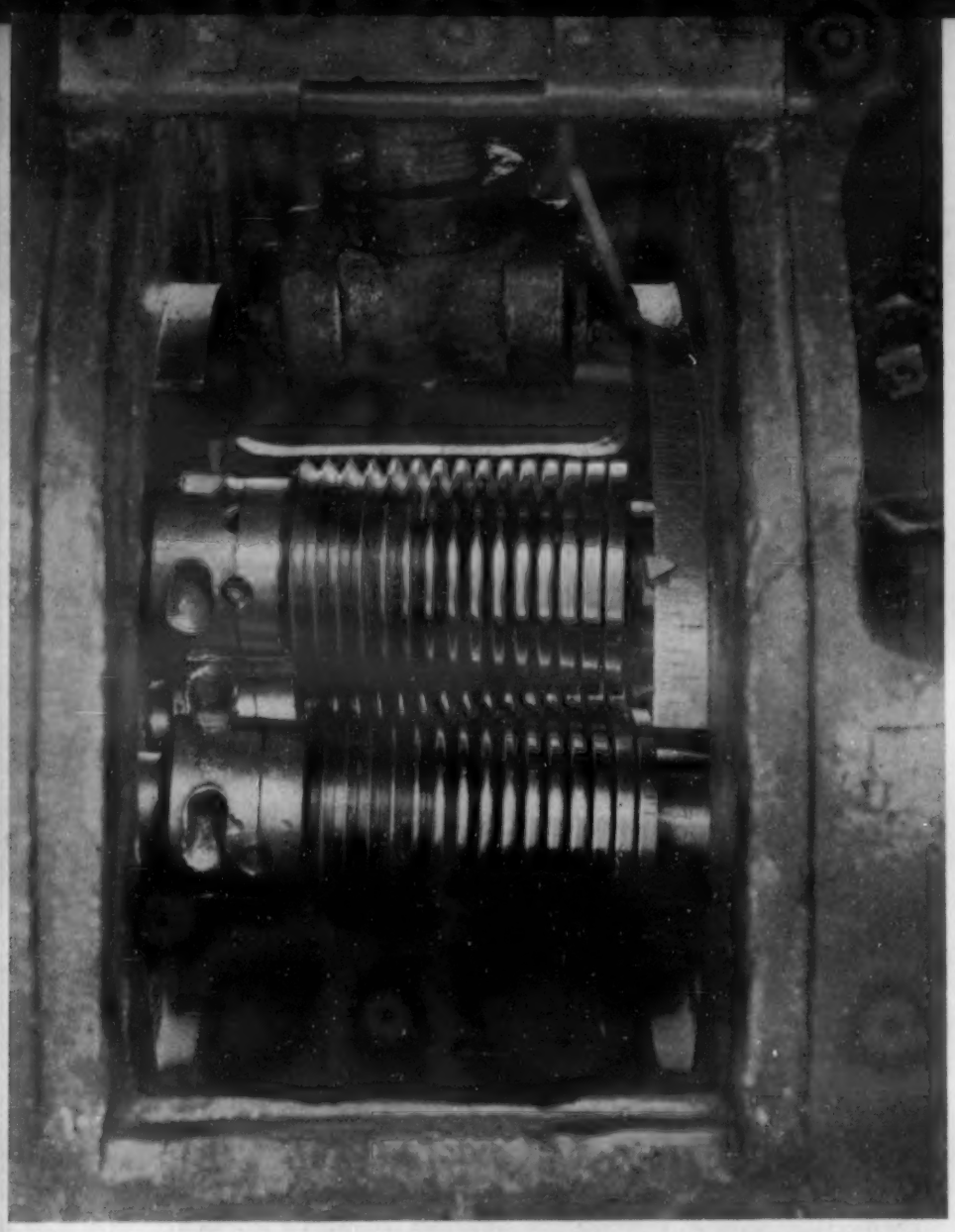
The metal in the tubing which is to be made into the finned product must possess properties adaptable to the process—ductility and formability without cracking, absence of excessive work hardening properties, uniformity in structure and capability for heat treatment.

Special Copper Used

In the case of copper for finned tubing, oxygen-free, high-conductivity "OFHC" copper[1], as made by the United States Metals Refining Co., is peculiarly adapted to the new

Another View of the Method of Coiling Finned Tubing





The Special Machine on which is Produced Finned Metal Tubing in One Solid Piece

process. This is received at the plant in slugs or small round billets about 8 to 9 in. long and about 5 in. in diameter. These have been cut at the producer's plant from the regular, vertically cast, round billets.

These small billets are then manufactured into tubes. The billets are heated to the proper extrusion temperature (1350 deg. F.) in an oil-fired muffle type furnace having a reducing atmosphere. The tubes, as they come from the extruder, are immediately straightened by hand manipulation and then quenched in water.

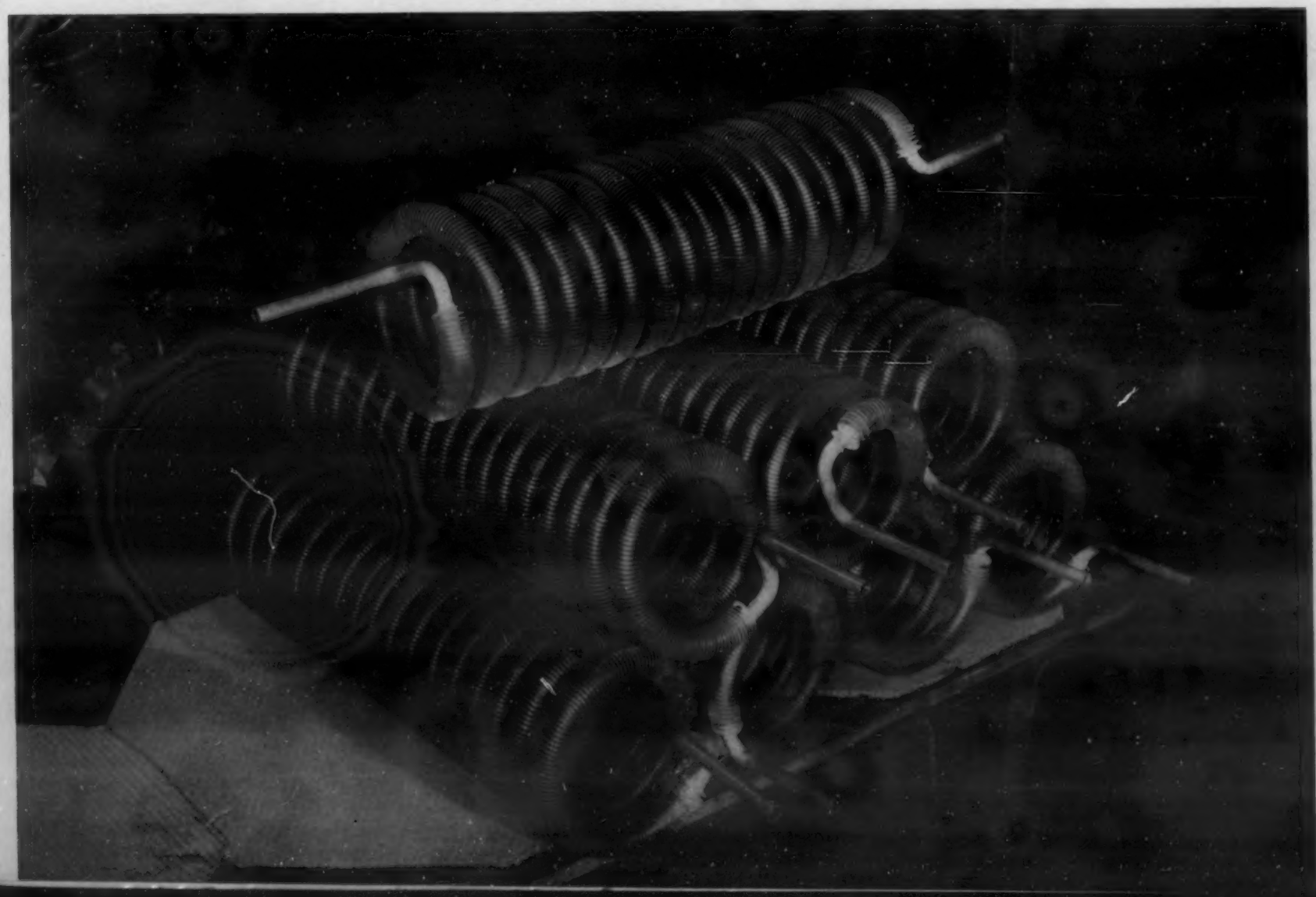
These extruded tubes are then drawn to size. A definite base size tube is necessary for running through the finning machine. The dimensions are regulated by the type and size of finned product to be made, whether of copper or aluminum. The dies through which the base size tubes are extruded or drawn are usually of tungsten carbide though for certain purposes a high-carbon steel die is used.

Controlled Atmosphere Furnace for Annealing

The next step in the process is to anneal to dead softness the base size tubes before finning. This is accomplished in a controlled atmosphere furnace. The furnace used is a large one, made by the General Electric Co. The annealing must be accomplished in an atmosphere free from oxygen, made by burning a mixture of 8½ parts of air with 1 part of natural gas. The product is free from oxygen but contains some sulphur and moisture which must be removed. The inorganic sulphur is removed by passing the gas through iron oxide. The gas is then sent through cooling coils to remove the organic sulphur that remains and also the moisture. Thus the gas is in turn freed from oxygen, sulphur and moisture. It enters the furnace at the rate of about 4500 cu. ft. per hr.—sufficient to insure a slight pressure and prevent the entrance of outside air.

Coiled tubing, before it enters another General Electric annealing furnace (controlled for a different speed and heat than for straight lengths) is purged with this same gas, admitted under a pressure of about 25 lbs. per sq. in.

A Group of Coils of Finned Copper Tubing



Straight tubes are self-purged, due to the stack effect and the excess pressure inside the furnace. The resistor elements are located above and below the alloy mesh belt which transports the tubes through the furnace. A series of fans throughout the heating chamber assures uniform temperature distribution and more rapid heat transfer. In the case of base size copper tubes for manufacture into finned tubing, the temperature of the tubing is 1050 deg. F., the furnace temperature reaching 1200 deg. F.

The cooling zone of the furnace also contains the special atmosphere to prevent oxidation or tarnishing. The tubes emerge from the heating zone of the furnace and enter the cooling section which is roughly twice the length of the heating zone. This cooling zone is also equipped with fans to accelerate the cooling. In this the tubes fall to approximately room temperature. The speed of passage of the material through the furnace is accommodated to the temperature and the metal involved.

The tubes, as they come from the bright annealing furnace in a dead soft condition, are ready for the finning machine, and are there made into the finned product known as "All-In-One Finned Tubing." The fins on the finished product have a full hardness of Rockwell B 60. There is a definite relation between the dimensions of the base size tubes and the finned product, whether copper or aluminum.

Pure Al for Aluminum Tubes

In the case of the manufacture of finned aluminum tubes, the metal used is commercially pure aluminum (2S). This is subjected to the same manufacturing and annealing operations except that the temperature in the bright annealing furnace is kept down to 1000 deg., F., the metal reaching 850 deg. F.

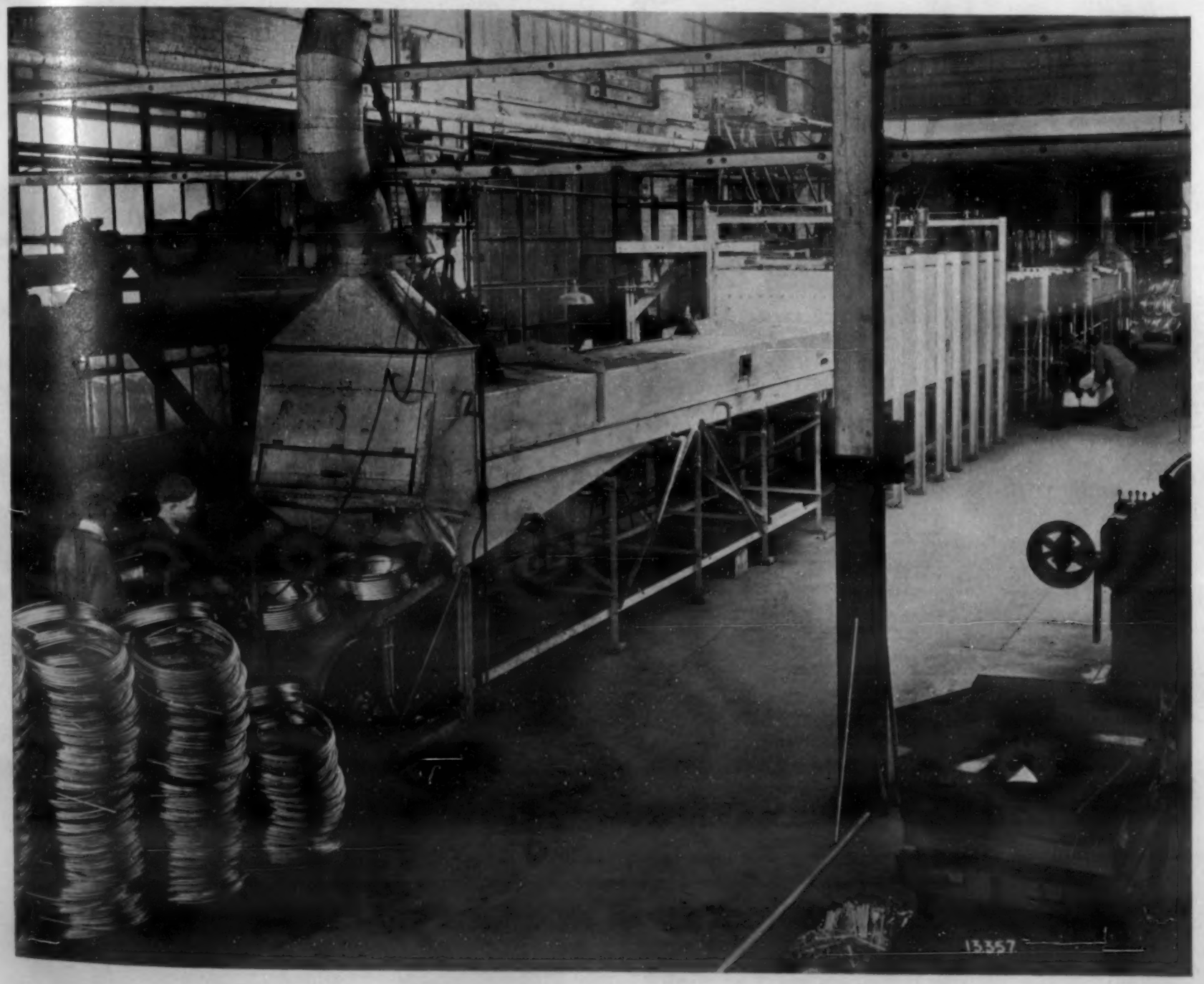
The finned tubing produced as described, if it is to be used in the form of a coil or in any shape requiring bending, must be annealed to reduce the hardness produced by the cold working. This is done in the same bright annealing furnace already described and under the same conditions for either copper or aluminum. The finned product is sold either in straight sections, which also may be annealed if specified, or in coils as illustrated.

Thus there is produced, on a large scale and by a comparatively simple process, finned tubing of copper or aluminum which surpasses in decided measure the products made by earlier processes.

Reference

[1] "The Manufacture of Oxygen-Free, High-Conductivity Copper," Edwin F. Cone, METALS AND ALLOYS, Vol. 8, February, 1937, pp. 33-37.

The Controlled Atmosphere Furnace for Bright Annealing Finned Metal Tubing



ALUMINUM
FROM THE
Ore to Final Product

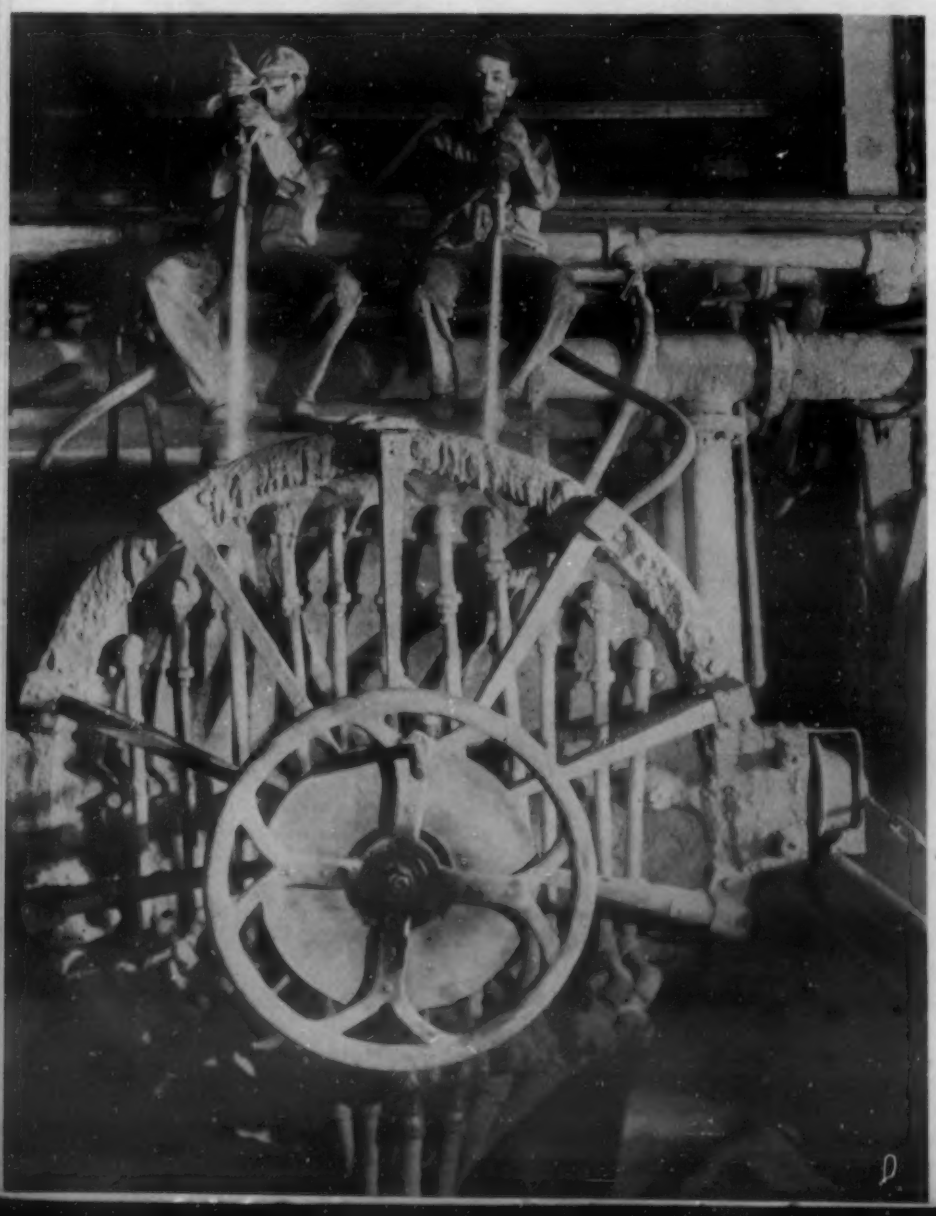
Photos by MARGARET BOURKE-WHITE

Courtesy Aluminum Co. of America

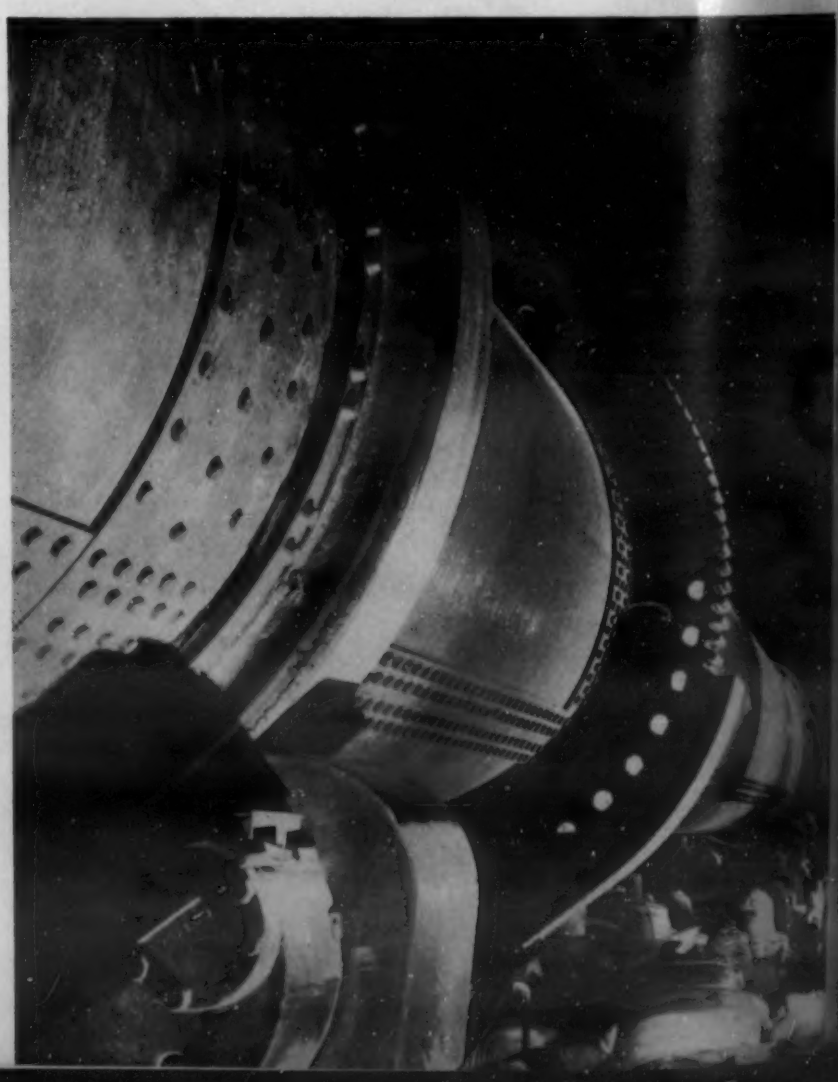
Mining Bauxite, the Ore of Aluminum, by Open Pit Methods.

Another Step in the Purification of Bauxite. Pumping the Sodium Aluminate Solution into a Precipitator.

A Step in the Purification of Bauxite. Filtering the impurities out of the sodium aluminate solution.



To Change Aluminum Hydroxide into Aluminum Oxide, the Hydroxide Is Heated White Hot in Large Rotating Kilns.

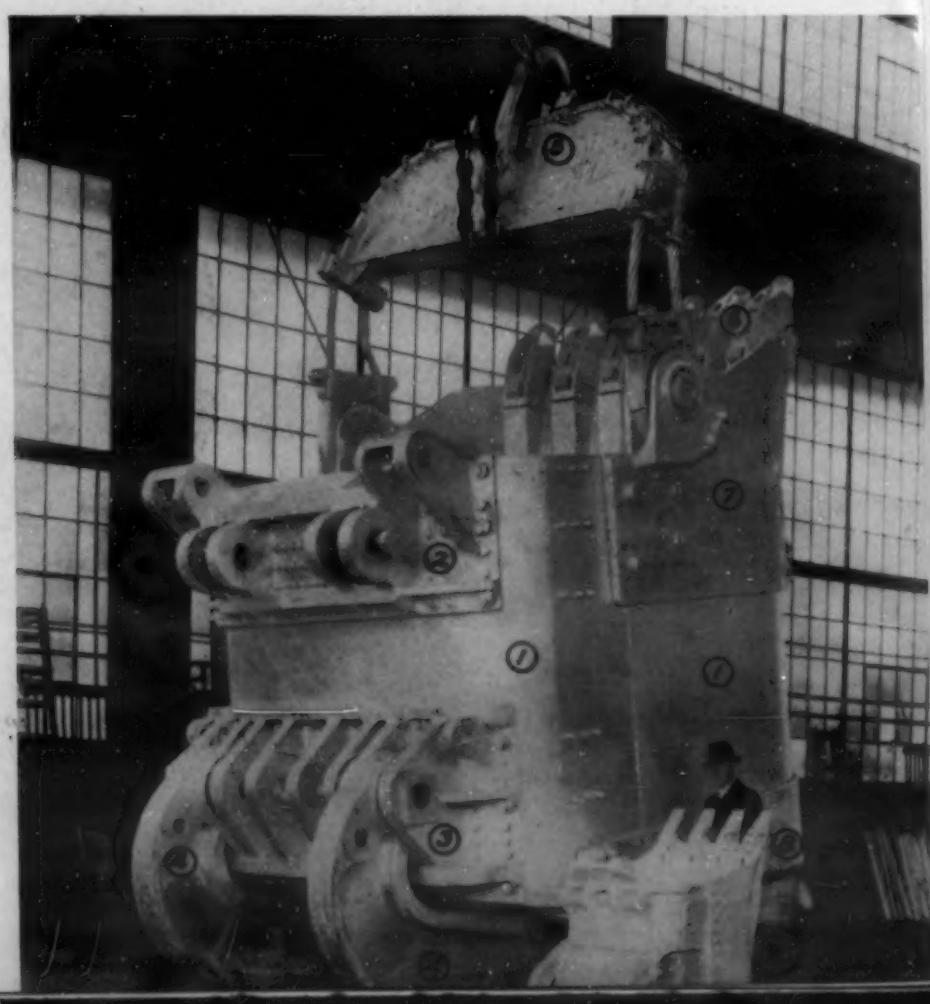


Pouring Aluminum Pigs in a Reduction Works.

Coiling and Shearing Strip Sheet

Rolling Aluminum Sheet

(Bottom) The Largest Power Shovel Dipper ever Built—32 Cu. Yd. Capacity It is made principally of aluminum alloys as follows: (1). Shell plates (alumi num alloy rolled plate). (2). Top back pad casting (heat-treated aluminun alloy casting). (3). Bottom back pad casting (heat-treated aluminum alloy cast ing). (4) Hinges (heat-treated aluminum alloy casting). (5). Bail (aluminun and steel alloys). (6). Teeth (manganese steel). (7). Cutting lip (manganes steel). (8) Bottom band (manganese steel). The light-weight dipper ha about 30 per cent larger capacity than a conventional dipper for the sam machine. It was manufactured by Marion Steam Shovel Co., for Norther Illinois Coal Corp. It has been in service since November, 1935, is still i perfect condition, and has required no repairs.



Diffusion in Solid Metals—I

A CORRELATED ABSTRACT

by A. I. Krynitsky

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(Publication Approved by the Directors)

The part which diffusion plays in the behavior of alloys is of such importance that it is remarkable that so little attention has been given to its study.—W. Rosenhain.[1]

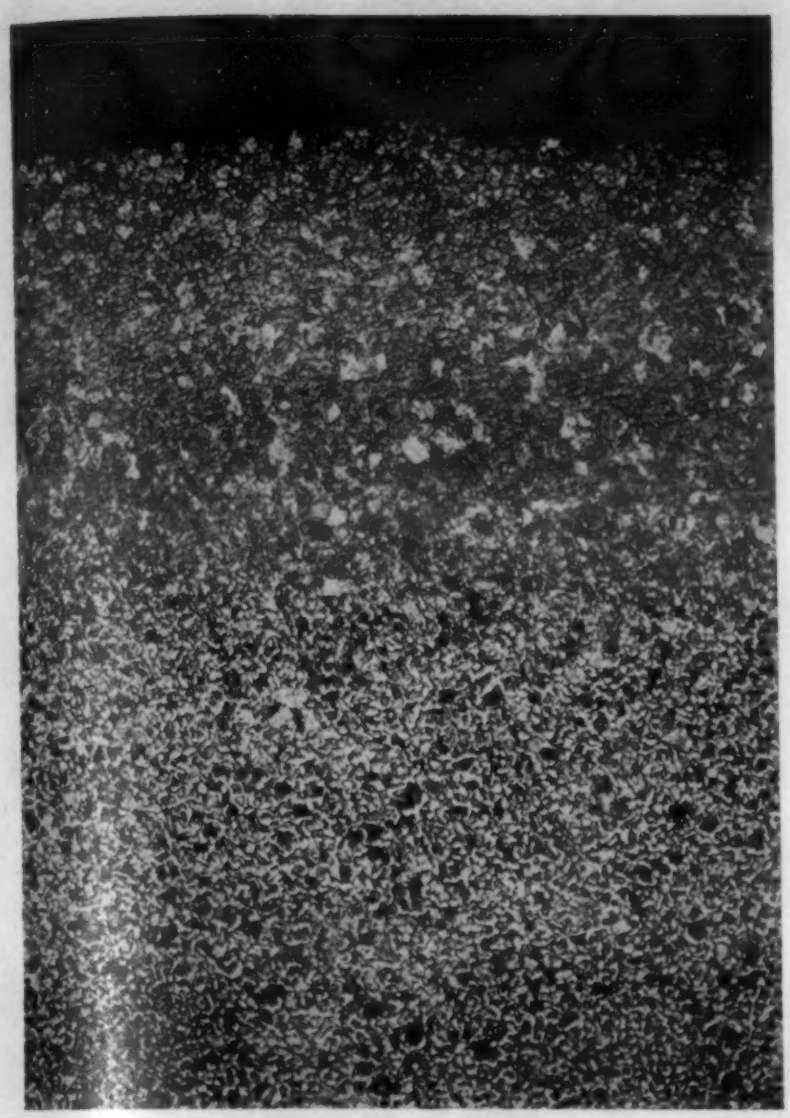
IN SPITE OF MANY INVESTIGATIONS made on this subject, the diffusion phenomena in solid metals still seem to be very far from being solved. The reason for this evidently is that diffusion in many cases is a much more complicated process than is usually assumed, and apparently is very intimately connected with the crystalline and atomic structures of metals. If one only recalls the amount of work which was done and still is carried on to explain the nature of martensite and the hardness phenomena in general, he will readily see how little study has been devoted to explain the mechanism of diffusion in solids, which is certainly a no less complicated problem than the two just mentioned. Although it is difficult to form at present a clear conception of this problem, the results obtained thus far are of such theoretical and practical importance that they seem to justify an attempt to make a correlated abstract on this subject.

Early Experiments on Diffusion in Metals

A COMPREHENSIVE SUMMARY with a number of references on "Diffusion in Solids" was published by Desch[2] in 1912. According to him the earliest scientific record of the production of an alloy by union in the solid state appears to be an observation by Faraday and Stodart that iron and platinum can be alloyed by welding at a temperature below that at which fusion can take place. A solid solution is formed in this case. It was shown by Tchernoff[3] in 1868 that, if two surfaces of steel of the same nature be placed in intimate contact and heated above the A_3 point, they will unite.

The earliest systematic investigation of diffusion in the solid states is due to Spring[4]. It was observed by him (1882) that various powdered solids could be formed into a compact mass by the application of high pressure at ordi-

The Effect of Time is Familiar in Respect to the Depth of Case of Carburized Objects. The macrographs, all at 10 diameters, show (left) metal heated at 1550 deg. F. per ½ hr., (center) heated at 1580 deg. F. for 1 and (right) heated at 1550 deg. F. for 2 hrs. In liquid baths, using cyanides as the active agents, both carbon and nitrogen are introduced into the surface. The carbon diffuses the faster, so the case has a sharper gradient as to nitrogen than it has as to carbon. The macrographs show a gradual increase of penetration of case in samples of steel held in the carburizing bath for different periods of time.



S. A. E. 3140, Gas Carburized 3 hrs. at 1600 deg. F. Magnification 100 X (Courtesy: Surface Combustion Co.)

With the proper atmosphere to supply carbon at the rate at which it can be diffused into the core, the proper time and temperature, smooth blending of case and core can be obtained.

nary temperature. In 1909 these experiments of Spring were extended by Masing[3a] who compressed mixtures of the filings of various pairs of metals in a steel cylinder under pressure of 1,000 to 5,000 atmospheres. With the help of thermoanalysis, metallographic examination, and measurement of electrical resistivity he estimated, the extent to which union had taken place after heating these mixtures to different temperatures and for different periods of time. Masing found that pressure alone had no influence on diffusion and served only to bring the fragments of the two metals into intimate contact.

In the further experiments of Spring[4], two cylinders of the same metal (see Table 1), accurately faced and

Table 1—Experiments of Spring on Diffusion in Cylinders Made of the Same Metal and Brought into Intimate Contact.

Metals	Temperature, Deg. C.	Duration of heating, Hrs.
Sb	395	12
Al	418	8
Cd	295	5
Bi	240	7
Cu	403	8
Sn	190	8
Au	400	4
Pt	400	4
Pb	300	6
Zn	385	3

cleaned from grease, were found to adhere firmly when pressed together at ordinary temperatures and to become fully united on heating. Union occurred with all the metals examined, with the exception of an antimony, and was usually so intimate that when the two cylinders were subsequently separated by force the fracture passed through the metal on one side or the other of the plane of junction.

The first quantitative investigation on the mutual penetration of metals in the solid state was reported by Roberts-Austen[5] in his famous Bakerian lecture in 1896. In these experiments discs of gold or of alloy of lead with 5 per cent of gold were accurately faced and pressed into contact with cylinders of pure lead. The specimens were then kept at constant temperature for several weeks, and the diffusion was measured by cutting the lead cylinder into discs and estimating the proportion of gold in each disc. The gold alloy was placed at the base of the lead cylinder and diffusion took place against gravity. The following results (Table 2) were obtained after heating at 165 deg. C.

Table 2—Diffusion of Gold in Lead after Heating at 165 deg. C. for 30 days, expressed in sq. cm. per day.

No. of section from base	Weight of section, g	Gold, per cent	Diffusivity, sq. cm. day
1	0.64	0.039	....
2	2.33	0.030	0.005
3	2.02	0.015	....

for 30 days (Experiment No. 1). The higher the temperature the greater were the values for the diffusivity (Table 3).

Table 3—Diffusivity of Gold into Solid Lead.

Temperature of heating, Deg. C.	Diffusivity expressed in sq. cm. per day: Roberts-Austen, sq. cm. day	Diffusivity expressed in sq. cm. per day: Orstrand and Dewey, sq. cm. day
100	0.00002 0.00002	0.0002
150	.....	0.0043
165	0.004 0.005	.....
197	.....	0.0076
200	0.007 0.008	.....
251	0.023 0.030	.....
492	3.00 3.07	.....

The diffusivity in this table is expressed in square centimeters per day as calculated by means of Fick's law of diffusion. Fick's law states that *"The quantity of salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near each other."*

Fourier's theory of thermal conduction was applied by Fick to the phenomena of material diffusion generally. The movement in linear diffusion may be expressed by the differential equation:

$$\frac{dv}{dt} = k \frac{d^2v}{dx^2},$$

where x is the distance in the direction in which diffusion takes place; v is the degree of concentration of the diffusing metal, and t is the time. k is the diffusion constant, that is, the number which expresses the quantity of the metal, in grams, diffusing through unit area (1 sq. cm.) in unit time (one day) when the difference in concentration (grams per cubic centimeter) is maintained between the two sides of a layer one centimeter thick. The unit of diffusivity has the dimensions (L^2T^{-1}), so that diffusion constants may be expressed in square centimeters per day. The constant has a definite value for each pair of metals at a particular temperature.

Similar experiments were carried out by Roberts-Austen[6] at room temperature (around 18 deg. C.) for a period of four years. At the end of the four years the discs of gold were found to be adherent to the lead. The lead cylinders were divided into thin slices at right angles to the longitudinal axes. The first section was approximately 0.75

mm. thick, but the succeeding layers were about 2.3 mm. thick. Gold was found in each of the four slices, whereas only the minutest traces of gold could be found in any slice beyond the fourth from the base. Another experiment carried out by Roberts-Austen showed that the rate of diffusion of gold into solid silver at 800 deg. C. is of the same order as that of gold in lead at 200 deg. C.

Van Orstrand and Dewey[7], who (in 1915) repeated the experiments of Roberts-Austen on the diffusion of gold in solid lead at the temperatures of 100, 150, 180 and 197 deg. C., using greater refinements in measurements and calculations, found that Roberts-Austen's values of the coefficient of diffusion of gold into solid lead are practically correct except for the value at 100 deg. C., which is probably too small. They also found that the value of the coefficients probably increases with pressure.

Principles Governing Diffusion in Solid Metals

ALTHOUGH the mechanism of diffusion in solid metals was the subject of a great deal of study from many viewpoints by the recent investigators, the results obtained are hardly comparable as the experiments have been carried out under widely varying conditions. However, as far as can be judged from the data available at the present time, the following factors seem to be the most important in the occurrence of diffusion in solids.

Influence of Temperature

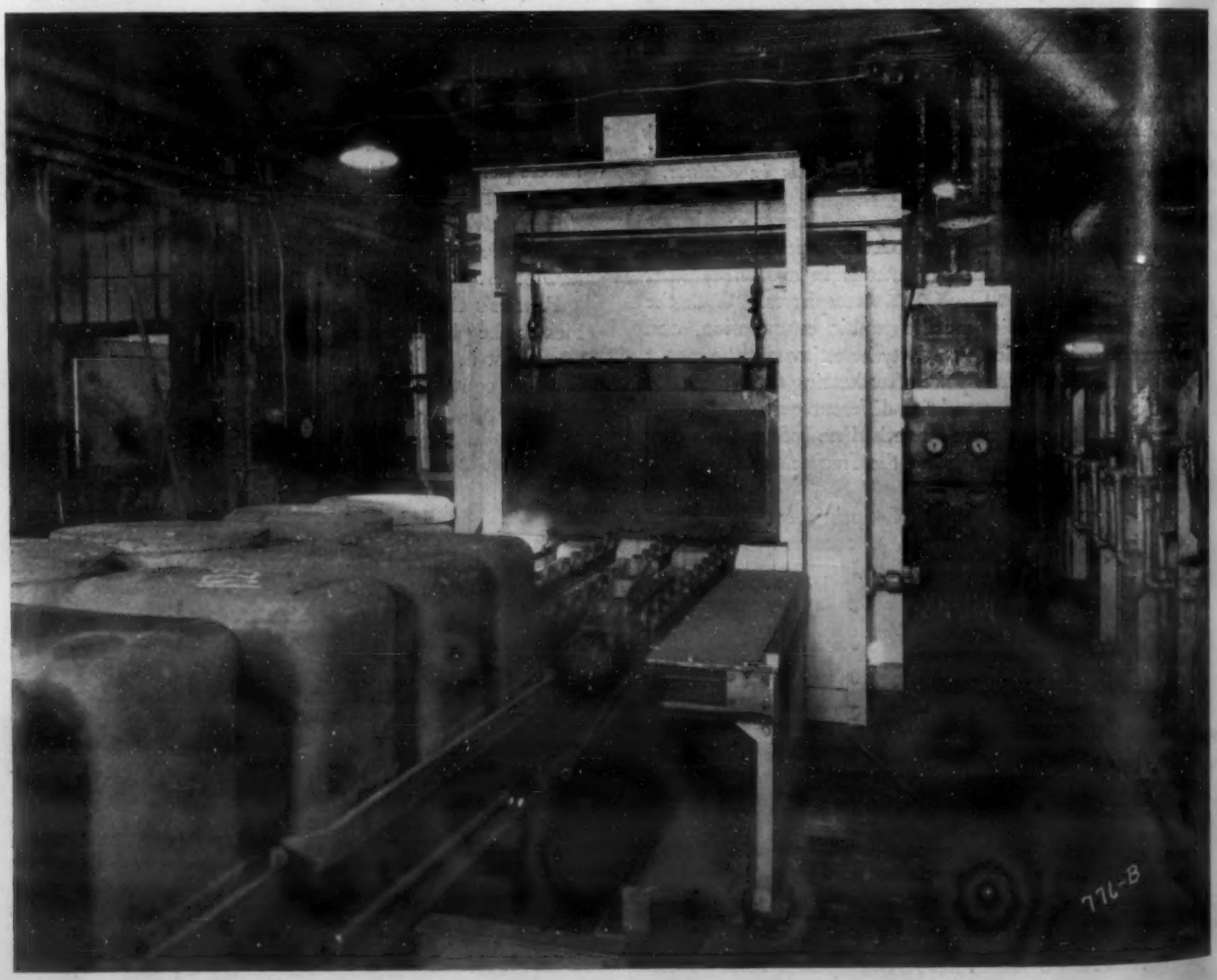
As the temperature is increased, the amplitude of the thermal oscillations increases and the rate of diffusion increases. The following expression for the diffusion coefficient was developed by Dushman and Langmuir[8]: $D = K d^2$, where d is distance between the layers of atoms of the solid and K is a frequency analogous to the velocity constant of unimolecular chemical reactions. The velocity of such reactions is approximately given by the semi-empirical relation:

$$K = \frac{Ql}{Nh} e^{-Q/RT}$$

According to their calculations there is a linear relation between log D and $\frac{1}{T}$, where T is the absolute temperature.

A very extensive investigation on diffusion in solid metals was carried out by Weiss[9]. In his study of the diffusivity-temperature relation, in order to eliminate certain factors such as irregularity of contact and mechanical distortion, Weiss used a silver-antimony alloy containing

Continuous Pusher Type Furnace for Case-Hardening with Solid Carburizer (Courtesy: The Electric Furnace Co.)



14 per cent of antimony. In the state of equilibrium this alloy is a homogeneous solid solution. Under certain conditions, however, it may be brought into a state of heterogeneous solution containing dendrites of Ag_3Sb, which are colored violet when etched with ferric chloride solution. During annealing this constituent is dissolved in the matrix and disappears entirely. The time in which it disappears may be established with the aid of a microscope very accurately.

A number of specimens of such heterogeneous alloy were prepared. They were heated at different temperatures and for different periods of time until the moment of disappearance of the Ag_3Sb constituent. Comparison of the velocities or homogenization at different temperatures permitted the establishment of the following relation:

$$v = \frac{1}{\theta} = K a^T, \qquad \text{where v is}$$

the rate of diffusion, and equivalent to the reciprocal of time; θ is time; and T is absolute temperature. a and K are constants which must be determined experimentally.

The formula above may also be written: $\ln v = \ln K + T \ln a$ and represents the straight-line relation where $\ln a$ determines the slope of the straight line. This relation was recently confirmed by Ageew and Vher[10] by their experiments on the diffusion of aluminum in iron (containing 0.15 per cent of C), carried on in an atmosphere of nitrogen at 1,000 to 1,100 deg. C. Strictly speaking, v in the equation above is the rate of solution and not the rate of diffusion but it is thought that the process of homogenization of alloys requires diffusion and it seems of significance that the exponential relationship established experimentally by Weiss is very similar to the Dushman-Langmuir equation.

A very interesting contribution to the subject was presented by Seith and Laird[11]. These authors have studied the diffusion into lead of silver, bismuth, thallium and tin. They express their results in the form of Van t Hoff's equation:

$$D = Ae^{-Q/RT} \text{ or } \ln D = \ln A - \frac{Q}{RT}$$

If $\ln D$ is plotted against $\frac{1}{T}$, a series of straight lines is obtained which represent both the rate of diffusion at any given temperature and the change of that rate with change of temperature.

Plotting the logarithm of the amount of zinc diffused into copper per unit area ($\ln \triangle w$) against the reciprocal of the absolute temperature $\left(\frac{1}{T}\right)$ Yoshito Yamauchi[12] obtained for both cast and rolled copper straight lines and expressed the relation between $\triangle w$ and T by the following formula:

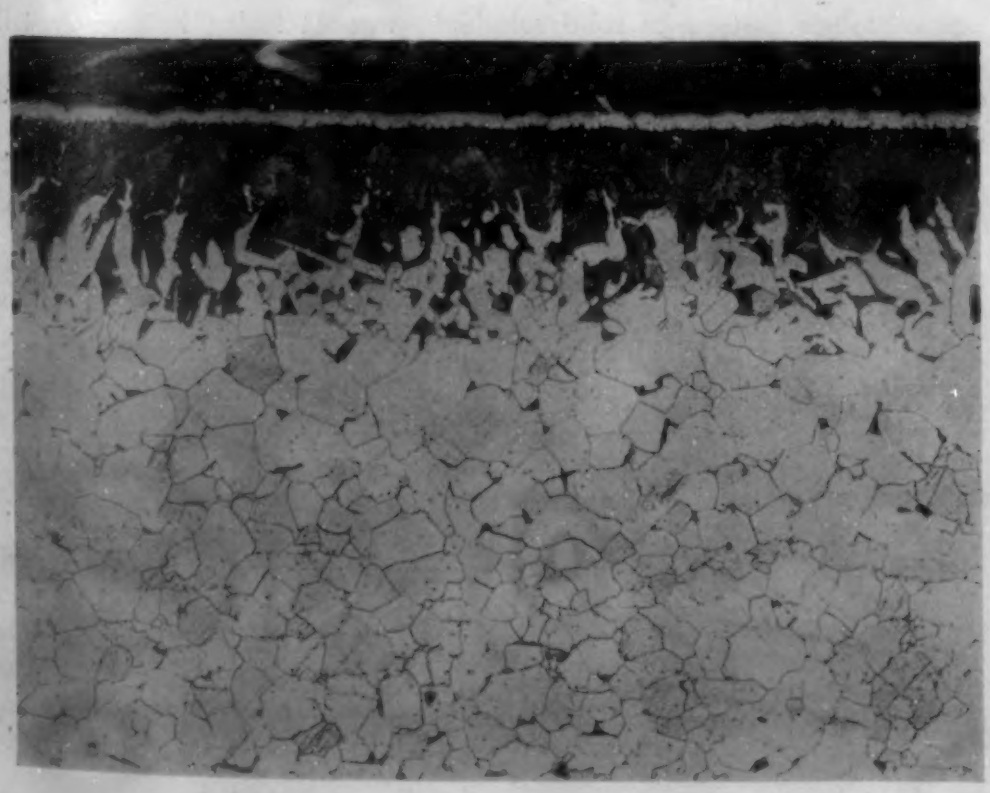
$$\triangle w = Ae^{-\frac{B}{T}}$$

where A and B are constants. It was found that at low temperatures the amount of zinc diffused per unit area gives lower values for rolled copper than for cast copper.

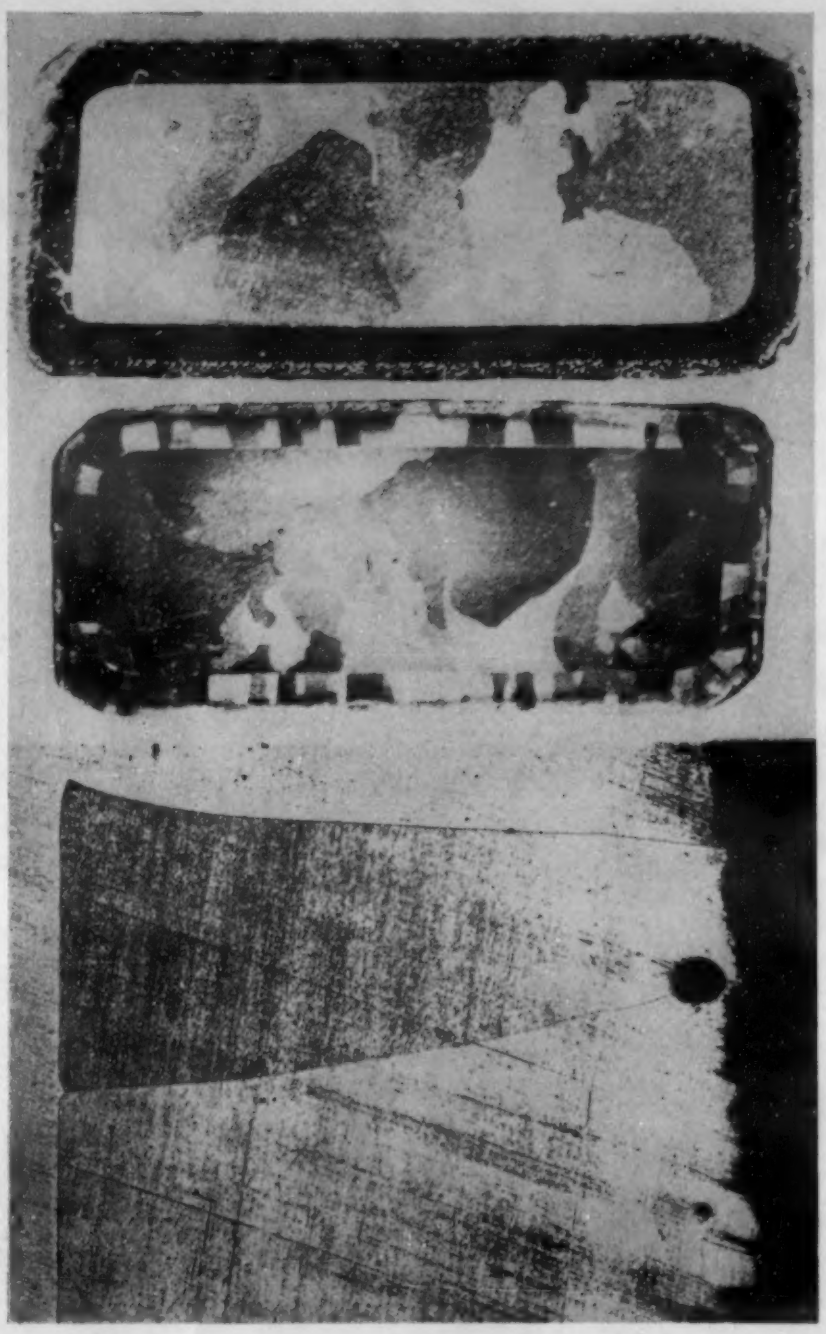
As the temperature rises, however, the former gradually approaches the latter, with the removal of stresses owing to the recrystallization, so that both give the same value at about 600 deg. C. Van Liempt[12a] found that the diffusivity of molybdenum into tungsten varies approximately as the 19th power of the temperature. In comparing now the results obtained on the diffusivity-temperature relation by different investigators, it is doubtful whether one formula can be developed which will hold good for all cases of diffusion in solid metals. It seems, however, that the Dushman-Langmuir equation is probably more nearly correct interpretation of the diffusion phenomena.

The Manner In Which Diffusion Takes Place

It appears that penetration of one metal into another may be accomplished in the following manners: (1) By migration along the crystal boundaries, (2) by transfer through the solid solution, and (3) by formation of an intermetallic compound. Such a division is here considered only for convenience in further discussions.



This Specimen Was Carburized in a Properly Carburizing Atmosphere and then Heated in a Decarburizing Atmosphere. The carbon diffused inward during carburizing, but when the surface began to be depleted in carbon, it diffused both inward and outward, illustrating the dependence of diffusion upon a concentration gradient. Specimen etched with nital. Magnification 100 X. (Courtesy: Hevi Duty Electric Co.)



Cross Section of Fe-Cr Specimen after Diffusion Had Taken Place. Top—Etched with nital. Magnification 5 X. Center—Etched with $FeCl_3$ + HCl. Magnification 5 X. Bottom—Etched with $FeCl_3$ + HCl. Magnification 10 X. When the boundary line between he two zones crosses a grain boundary between the columnar grains, a pronounced V is formed, the apex extending away from the coarse-grained material in the interior. This phenomenon was found consistently. The boundary line seems to be lacking at the upper left-hand side of this photomicrograph.

7. Diffusion by migration along the crystal boundaries.

The entering element has to get through somehow, and the general hypothesis is that diffusion may occur along the crystal boundaries, as has been shown for the diffusion of thorium through tungsten filaments, and observed by Desch[13] in his experiments with zinc and polycrystalline copper, carried out at low temperatures. In practically all cases examined he found a narrow band of alpha-constituent running along the crystal boundaries.

It is known that the solubility of carbon in alpha iron does not exceed 0.035 per cent at 700 deg. C. and falls to less than 0.01 per cent at room temperature. On the other hand the migration of carbide takes place freely in the neighborhood of 630 deg. C. The result of this is that carbide segregates along the crystal boundaries or is deposited on already existing crystals of cementite if the temperature is maintained below the critical point.

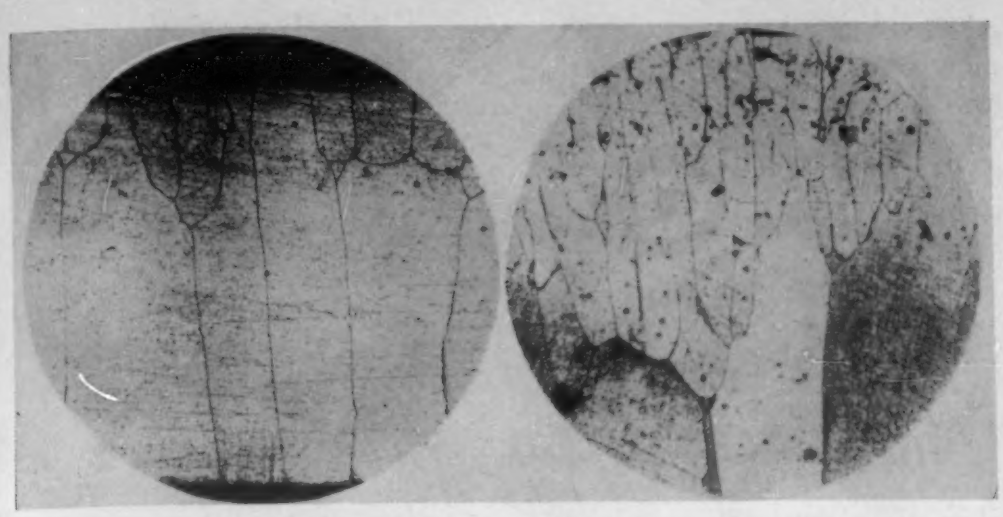
It was found by Sakharova[14] in her investigation on the diffusion of copper into commercial iron at 1,300 deg. C. that copper or a solid solution of iron in copper diffused between the crystals of ferrite.

2. Diffusion by transfer through solid solution.

In his excellent discussion on this subject, Desch[15] states that it "is necessary for diffusion through a space lattice that the two elements shall be capable of forming solid solution with each other." This means that the solvent must be able to accommodate the "stranger" atoms, either on points of its own lattice (substantial type of solid solution) or in the interstices between (interstitial type of solid solution), without losing its own crystallographic identity.

There is a great number of observations relating to the formation of solid solution by the process of diffusion. Some of these observations will be briefly described below. It has been observed that a layer of silver, deposited on copper, may be absorbed by the copper in course of time if it is sufficiently thin[2]. As copper is capable of dissolving about 5 per cent of silver in the solid state, absorption will cease when this concentration has been reached. It has been suggested[16] that the absorption might be hindered by interposition of a thin layer of electrolytic iron, in which silver is not soluble to a measurable extent.

When nickel wire 0.5 cm. in diameter was coated with copper to form a compound wire containing 59 per cent of Cu and 41 per cent of Ni and then heated to 1,000 deg. C. in hydrogen[17], a slight increase of electrical conductivity was noticed in the first hour because of the conversion of electrolytic copper into the better-conducting annealed form, but after this there was a continuous de-



Micrographs Showing Columnar Structure Produced by Diffusion of Chromium in Iron. Cold-rolled iron (left) chromized at 1300 to 1350 deg. C. for 4 hrs. Magnification 70 X. Cold-rolled iron (right) chromized at 1300 to 1350 deg. C. for 8 hrs. Magnification 42 X.

crease in conductivity. The minimum conductivity was reached after 140 hrs. of heating, when the value attained was exactly that of a homogeneous alloy of the same (59 per cent of Cu + 41 per cent of Ni) composition. Similar results were obtained when gold wires were coated with silver or copper.

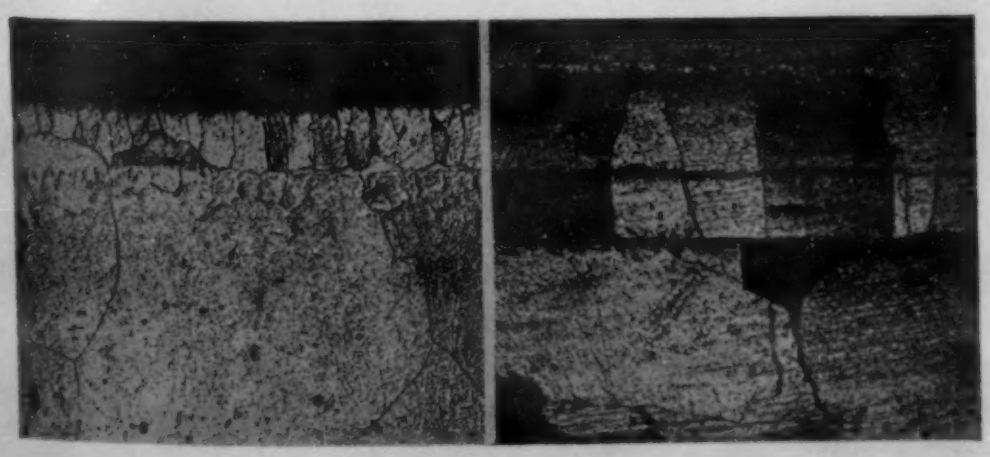
A very interesting case of diffusion of copper in pure aluminum has been recently observed by Burkhardt and Sachs[18]. The sheets of aluminum alloy containing 4 per cent of copper and 2 per cent of silicon, 1 mm. thick, clad with pure aluminum 0.05 mm. thick, were heated to 500 deg. C. for 12, and 25 mins. and quenched in water. The surface was then etched off in steps of 0.005 mm. and the sheets were examined by the X-ray method for the determination of the lattice constants. The outside surface showed only the sharp lines of pure aluminum; a little deeper the lines spread, which indicated a diffusion of copper alloy into the pure aluminum. After the diffusion layer was completely etched away, the sharp lines of the Al-Cu-Si alloy appeared. Graphs of the lattice constant at various depths indicated that after 25 mins. of heating at 500 deg. C. a pure aluminum layer slightly more than 0.02 mm. thick remained on the surface; beyond this it was contaminated with copper. It is estimated that after 2 or 3 hrs. of heating the copper would diffuse to the outside surface and the corrosion-protection would be lost. X-ray results were verified by microscopic examination and measurement.

It was also found that alloys containing magnesium (Duraluminum, Bondur) behaved with respect to the diffusion of copper in clad sheet as those free from magnesium. When a specimen of Armco iron was brought into close contact with very pure tin and the whole assembly was heated for 20 hrs. at the temperature of 1,050 deg. C., slowly cooled, sectioned, and examined under a microscope, there was a band of columnar crystals commencing at the tin interface and penetrating into the main mass of iron. It was shown that this band consisted of a solid solution of tin in iron and was a result of diffusion of tin into iron. It was also found that in every case the columnar structure was produced only on heating above the AC_3 point and no evidence of diffusion of tin into iron was observed below that point[19].

A similar structure, consisting of a border of columnar grains ending in a sharp boundary line, was observed by Grübe in his study of the diffusion of chromium into iron[20], and in some other systems[21].

The same observation was made by Kelley[23]. According to him, it seems to be a general law, whenever two metals are brought into intimate contact at a temperature at which diffusion takes place, that a comparatively rapid, or abnormal, grain-growth results. The grains are nearly always oriented with their long axes parallel to the direction of diffusion. He pointed out that the boundary line does not consistently cross all grains, and suggested that where the boundary line does not occur the interior grains had the same orientation as that assumed by the columnar grains. An excellent illustration of the columnar structure produced by the diffusion of chromium into iron is given by Hicks[22]. The boundary line dividing the interior portion of the specimen of iron from the outer zone of columnar crystals is perfectly sharp and follows the outer contour of the specimen remarkably. In some crystals, however, this boundary line was lacking, which fact is in agreement with the above observation of Kelley.

According to Jones[24] when the element *b* diffuses into



Armco Iron (left) Heated in Chromium. Magnification 200 X. Armco Iron (right) Heated in Chromium Twice as Long as Sample Shown at Left. Magnification 100 X.

Comparison of these photomicrographs indicates that, on longer heating, the columnar grains may grow in width as well as in depth. The sharp line usually found between columnar-grained zone and the core is of considerable interest.

metal *a*, it will do so with the production of one or two possible effects: Either (1) the atoms of *b* will accept the lattice of *a* and will thus produce a solid solution a_1 or (2) the diffusing atoms of *b* will saturate the existing lattice of *a*, and a new phase, a_2, will be formed. If a_2 also has a range of solubility for *b*, and if the supply of *b* by diffusion through a_1 be sufficient to maintain the requisite concentration, then a boundary will be perceived in the micro-structure, which marks the transition of the phase a_1 to a_2. Such a boundary line lying in a diffusion zone is therefore invariably an evidence of phase change.

Jones describes this boundary line as a "diffusion boundary" and divides the elements diffusing into iron into two groups: The elements of the first (Al, Sb, As, Be, Cr, Mo, P, Si, Sn, Ti, W, U, V, Zn), when allowed to diffuse into iron at temperatures between 1,000 and 1,300 deg. C., do so by the production of a "diffusion boundary" and a columnar diffusion growth of ferrite. It is to be presumed, therefore, that the binary system of each such element with iron includes a γ-loop, which, for instance, may be seen in the iron-chromium constitutional diagram of Adcock[25]. The elements of the second group (B, C, Co, Cu, Au, Ir, Ni, Mn, Ag), when allowed to diffuse into iron at temperatures between 1,000 and 1,300 deg. C., do not produce a "diffusion boundary". It is to be deduced, therefore, that each stabilizes the γ modification of iron.

3. Diffusion by formation of intermetallic compounds.

In his study of diffusion through the formation of zones of intermetallic compounds, Weiss[9] employed small cylinders made of different metals. One base of each cylinder was carefully polished. Two cylinders were then placed with slight friction in an iron tube lined with an asbestos sheet and their polished bases were brought mechanically into intimate contact with each other. The whole assembly then was heated at various temperatures, cooled, and sawn in half for microscopic examination. From his observations on the diffusion of Ag-Sb; Cu-Sb; Ag-Sb and Au-Sb, Weiss concluded that the results obtained can be expressed by the following equation:

$$\theta = bx^2$$

where θ is time, x is the thickness of a layer of the compound formed, and b is a constant.

A 70-30 Brass Annealed in Contact with Zinc for 56 Hrs. at 450 deg. C. Magnification 100 X. The lines dividing the diffusion zones between α and β, and β and γ, are as sharp as if scribed with a compass.

When an intermetallic compound is formed by diffusion the boundary of the new phase is perfectly sharp. That the β phase in the copper-zinc system does not break up into a eutectoid of α and γ at 470 deg. C. was proved by the diffusion of zinc into copper.

When a small cylinder of an alloy of 70 per cent of copper and 30 per cent of zinc was brought into close contact with zinc and the whole assembly was heated for 3 days at 420 to 430 deg. C., a layer of β phase was formed and was perfectly distinct[26]. *(To be Continued)*

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Steel Reminiscences—V

(Concluded from the last four issues)

by Henry D. Hibbard

Consulting Engineer, Plainfield, N. J.

MY FIRST KNOWLEDGE of manganese steel was in 1885 when at the Norway works. The manager, George Billings, showed me a small bar saying that it contained 9 per cent manganese. In my ignorance I corrected him saying, "You mean 0.90 per cent." "No," he replied, and I recoiled. It was made by Washburn in a small crucible steel plant at Allston, Mass. Hadfield had discovered and patented it, so Washburn knew of it and tried it out. The toughening imparted by heating and quenching was not mentioned at that time.

Early Manganese Steels

At Linden I made some manganese steel surreptitiously about 1889. I melted a quantity of ferromanganese in a crucible placed within the steel furnace, and then ran into the crucible from the ladle enough low carbon steel—about 30 lbs.—to give the desired proportion of manganese. After one or two failures, I made an ingot containing, as I recollect, about 11 per cent manganese.

One of the products made at Linden was cold-drawn shafting and the dies through which it was drawn failed too soon. I had my manganese steel ingot forged down to make a square cake about 7 in. x 7 in. x 2 in. thick. I said to the master mechanic, not knowing any better, "Now, if you can put a hole through this, it will make the best die you ever saw." "Oh!" said he, "I'll put a hole through it all right." But he didn't. He tried to for some hours but penetrated only a little way. Then he said, "It would be of no use to put a hole through it for I could not cut it out to the right size." We did not then know that extremely slow speed was necessary for cutting such steel as well as specially hardened drills. Manganese steel would not serve well in such a die as it flows too easily under pressure or impact in spite of its great resistance to cutting or wear.

Studied Hadfield Process in England

In 1891 I went to Sheffield, England, to study the Hadfield system for making steel castings, including manganese steel, for the Taylor Iron & Steel Co., High Bridge, N. J., who were Hadfield's licensees. We built a plant there for working the process which was started in 1893 at the beginning of a serious business depression brought on by, or at least following, Cleveland's Venezuela message. It was an unpropitious time to start a new business.

One thing that venture demonstrated was that the life of an English patent, 14 years, was far too short a time for the inventor of a thing at all revolutionary, or complicated, to profit much from it. It also showed that the conception and patenting of an invention, however good, is but a small step toward making a profit from it. The time, energy, and money expended in developing, manufacturing, and introducing it are the great things to that end. Manganese steel, being such a novel material, was but slowly introduced. Its great merit for purposes for which it was well suited militated against it. A salesman, almost in tears, exclaimed—"The damn stuff never wears out. You have to get a new customer every time you make a sale."

When showing manganese steel to a new "prospect," after its resistance to cutting and wear were understood, the inevitable question arose—"will it make a good cutting tool?" It was of no avail to say that it would not. But, as I said to one engineer, "As soon as I have gone, you will sneak down and have a tool made of it." He laughed but later confessed that he had done so, saying, "I could not understand why you would run down your own steel, but could not see why a steel so hard to cut would not make a good tool."

Joined A.I.M.E. in 1879

In 1879 I joined the American Institute of Mining Engineers and attended, in Montreal, Canada, my first meeting of that organization. To me it was a great event. Among the notables present were Eckley B. Coxe, president; T. M. Drown, secretary; Rossiter W. Raymond, founder and future secretary; Dr. T. Sterry Hunt, my former professor of geology; Prof. R. H. Richards, my teacher of mining; Alexander L. Holley, the leading steel-works engineer; and many others. Holley read a paper on washing pig iron at Krupp's works in Germany. Thirty years later I contributed to the Institute a second paper on that subject, dealing with the practice at Youngstown, O., far ahead of what Holley had described. Washed metal was sometimes sold on a guarantee of not over 0.006 per cent phosphorus, and heats were made containing but 0.001 per cent of that element.

One feature of the Montreal meeting was a visit to the British cruiser Tourmaline, which was visiting Montreal. Gilbert and Sullivan's operetta, "Pinafore," had just come out and was "all the rage," and everyone was eager to see

what a British warship was actually like. So, though it was not on the official program, the whole party went, much to the disgust of Dr. Hunt, who, because it interfered with his plans, declared it to be "madness."

Philadelphia Meeting of A.I.M.E.

In 1881 I attended a meeting of the Institute in Philadelphia. The speaking at the dinner, held at the Union League Club, was notable. The Hon. Wayne MacVeagh—afterward attorney-general of the United States—made a speech which raised burst after burst of laughter. I do not now remember a single point he made but enjoyed it hugely.

Then Raymond arose and all were at attention. There had been a fire in Secretary Drown's office at Lafayette College at Easton, Pa. Drown saved the *Transactions* of the Institute, but lost much of his own property, both books and apparatus, so a collection was taken up for him without his knowledge and Raymond made the presentation. He told the facts, declaring that it was like Drown to act so, and said that it was felt that something should be done about it, that some acknowledgment of Drown's unselfish action should be made. So it was decided to write a poem. He had the poem with him which he proceeded to read. It was:

To the Cashier of the Eleventh Ward Bank—
The subscriber would thank
You to pay down
To Thomas M. Drown
The sum which "follers,"
Three thousand dollars,
Yours with pleasure R,
W. Raymond, Treasurer.

That dinner was also memorable for the unique menu, prepared largely, if not wholly, by the late Persifor Frazer. Each item of food and of drink was accompanied by an apt mining or metallurgical quotation, many from members of the Institute. At the end, after the item "Toasts" was the quotation—"at this point the bosh begins" by T. F. Witherbee. Dr. Drown, in his affecting response to the poem, said, as he closed, that he would like to amend the menu by saying—"At *this* point the bosh begins," with accent on "this," which by raising a laugh relieved the situation.

At a New York meeting in 1884 Henry Ward Beecher attended as a friend of Raymond. In his talk he said that he did not claim to know much about mining, but perhaps he knew as much about it as the average miner knew of theology.

A 50-Yr. Member of A.I.M.E. and A.S.M.E.

In 1929 I became a 50-year member of the Institute and was awarded with three others, at the San Francisco meeting, the appropriate badge and diploma. In 1933 I also became a 50-year member of the American Society of Mechanical Engineers. I was then, and for three years, the only one to be a 50-year member in both of those national organizations.

With American Engineers in Europe

In 1889 I went to Europe with the first large party of engineers to make such a trip. In the party were about 300 including many members of the A.I.M.E. The main purpose was to see the World's Fair at Paris, and going in a body was because of an invitation from English engineers to do so, and to spend two weeks in England, where many social events were arranged for us. We dined with our hosts, seated alternately with them, in the Guildhall of London, the first time it had ever been used for other than State occasions.

A reception by Lord Brassey was superb. We did not however have time to examine his museum, collected by him from the whole world and housed in a three-story annex to his Park Lane house. I inanely remarked to his daughter, who received us, on the excellence of the music by a band of Italian singers whose tones were actually smothered by the buzz or roar of conversation. She, with perfect politeness, observed that they considered music to be an incentive to conversation.

At the diamond cutting works of his grandson, in London, I had a short talk with Sir Henry Bessemer. Answering my question, he said that he would probably never go to America, as his doctor thought the ocean voyage would be bad for him. I rejoined that, thanks to rails made of his steel—as all rails then were—he might some day be able to go all the way on cars, at which he smiled and said that he would like to do so.

At John Tyndall's Home

My best memory, is, however, of the day a limited number of us went by invitation to John Tyndall's home at Haslemere. I brought up the subject of the Matterhorn by commenting on a fine picture of that peak in his front hall, and he then told us of his unsuccessful attempt to scale it which had never been done. Lord Armstrong and Lord Carringford were there to assist in entertaining us. Lord Alfred Tennyson, who lived near, though invited by Tyndall, was not strong enough to attend.

The Exposition at Paris included no German exhibits. None were offered, and any offered would have been refused. The Eiffel Tower, built for the occasion, was the outstanding feature. A few of us ascended, partly by ladder, to Eiffel's studio about 100 ft. above the third or highest public platform. An exhibit of copper-bearing steels by Schneider, from the Creusot works, was notable among the metallurgical exhibits.

The steel people of Europe, it was said, suspected that we had come to learn their methods, and only a few were willing that we should visit their works, as a matter of fact there were only two or three steel men in the party. In Paris I saw a steel foundry with Robert converters making steel castings of excellent quality, mostly parts for mounting field artillery. In 1920 I again visited that plant. It was not far from the center of the city and a sort of nuisance to the neighborhood. Still they could not expel it but would not allow any extensions to be made.

Visited Some British Plants

In England I visited Jessops in Sheffield, and the Consett Iron Works where were eight siemas of about 10 tons capacity each. I visited two shipyards. One was that of Armstrong, Whitworth & Co. at Newcastle but they would not let me into their steelworks. I saw there, however, with interest, the largest steel ingots I ever saw up to then, and ingots poured in inclined molds. The purpose of slanting the mold was to allow the gases freer exit, but, as might have been expected, the practice was not continued.

The other shipyard was that of the Fairfield Shipbuilding Co., formerly John Elder & Co., on the Clyde near Glasgow. They built the largest ships of the period.

We returned home on the City of Paris which then held the record for speed in crossing the Atlantic. Thirty-one years later I crossed again on the same ship, then named the Philadelphia, on her last season. She had been wrecked at least once.

Progress in Development

Development from early days to the modern steel plant has been truly marvelous, and the end is not in sight, though perhaps the economic limit of size of furnace and mill has been reached. The blast furnace overdoes its function and the excesses of non-ferrous elements in crude iron are wasted.

A Letter from a Reader:

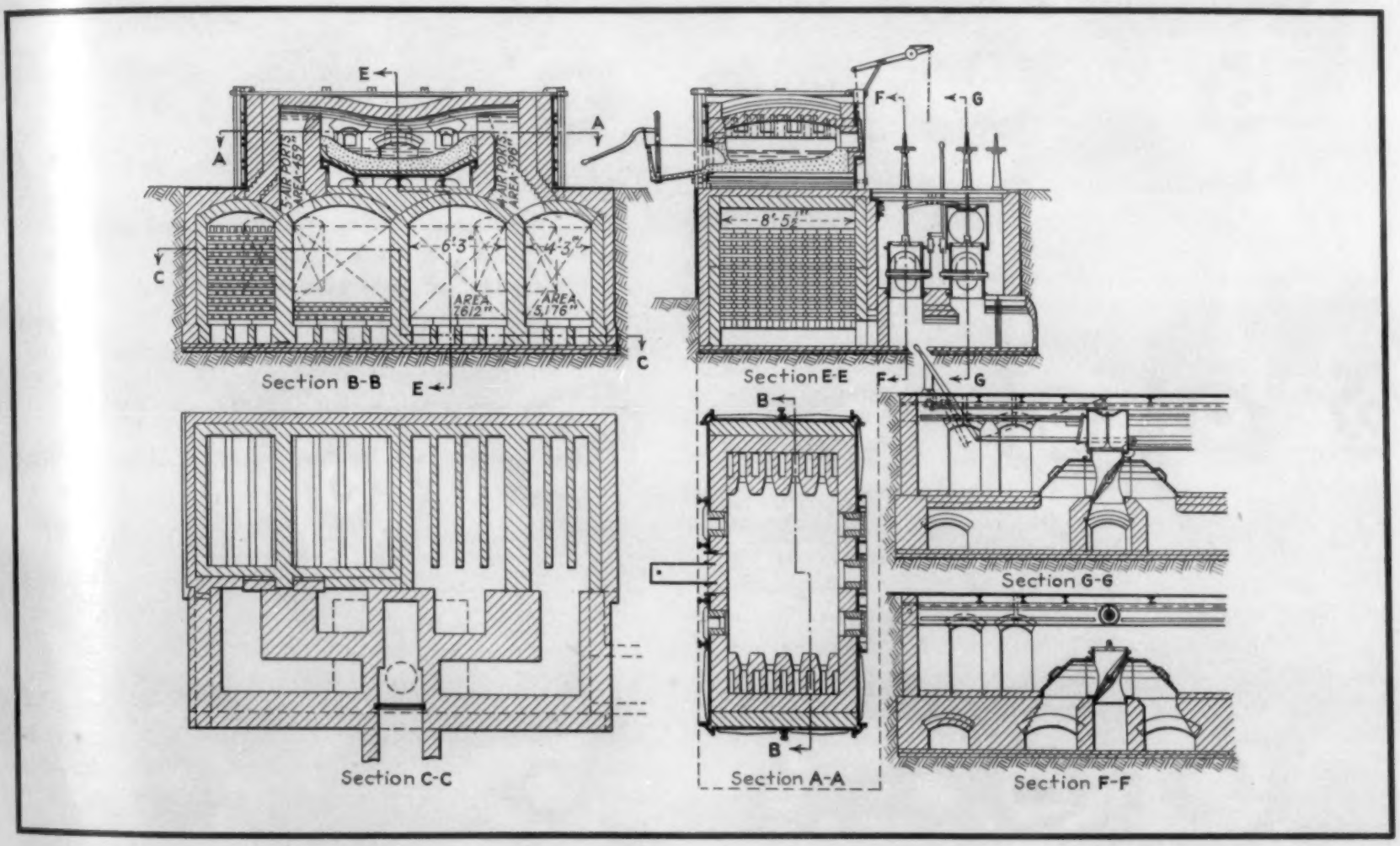
Through the courtesy of Mr. Hibbard, we are privileged to reproduce a letter received by him from John E. Galvin, president, Ohio Steel Foundry Co., Lima, Ohio. A reproduction of the open-hearth furnace, built in 1870, is also included.

Dear Mr. Hibbard:

I have been reading your "Steel Reminiscences" and I noted with much interest that you had visited the Bay State Iron Co. plant at South Boston, Mass., and had been chemist at the Nashua Iron & Steel Co. at Nashua, N. H.

Wellman's father was the general superintendent at the Nashua Iron & Steel Co. and I believe S. T. Wellman, Jr. designed this furnace for the Bay State Iron Works. Mr. Wellman afterwards left the Nashua Iron & Steel Co. to design and build the Otis Steel Co. plant at Cleveland. Later on he invented the open-hearth charging machine and numerous other appliances for steel works.

In addition, I am attaching a little pamphlet entitled "Forty-five Years of Open Hearth Practice", which was written by my father for the Inland Steel Co. safety magazine. * * * Before father died I asked him to write something about the men with whom he worked but before he got to it he passed away. Among these



My father worked at the Nashua Iron & Steel Co. as a boy. The last years of his life were spent as open-hearth superintendent for the Inland Steel Co. at Indiana Harbor, Ind. He died about four years ago at Long Beach, Calif., in his eighty-fourth year.

I am enclosing a photograph of a drawing of the Siemen's open-hearth furnace built for the Bay State Iron Works at Boston, Mass. in 1870. This photograph was made from a tracing made on May 12, 1915, from S. T. Wellman's drawing No. 2215. Mr. Wellman was the general superintendent at the Nashua Iron & Steel Co. and I believe S. T. Wellman, Jr. designed this furnace for the Bay State Iron Works. Mr. Wellman afterwards left the Nashua Iron & Steel Co. to design and build the Otis Steel Co. plant at Cleveland. Later on he invented the open-hearth charging machine and numerous other appliances for steel works.

In addition, I am attaching a little pamphlet entitled "Forty-five Years of Open Hearth Practice", which was written by my father for the Inland Steel Co. safety magazine. * * * Before father died I asked him to write something about the men with whom he worked but before he got to it he passed away. Among these men was Major Bent, general superintendent of the Pennsylvania Steel Co. plant in 1876, where father started up and operated their open-hearth furnaces. In that year Major Bent sent father and C. E. Stafford, who was the chemist there, to Europe, which trip is mentioned in this pamphlet.

Sincerely yours,

JOHN E. GALVIN

TITANIUM IMPROVES

Pearlitic Manganese Steel

by George F. Comstock

Metallurgist, Titanium Alloy Mfg. Co., Niagara Falls, N. Y.

Mr. Comstock, in making this a technical-minded rather than a sales-minded discussion, has refrained from emphasizing that the full benefit of titanium is not reached with the smaller additions such as have been used for purposes of deoxidation and degasification. This is probably the reason why the beneficial effect now found, was missed earlier, throughout the long period in which titanium additions have been made.

Another point, indicated by Steel No. 4 in the table, but not emphasized, is that it seems desirable to limit the sulphur to about 0.03 per cent in order to obtain the most benefit from titanium on ductility and impact, so that the addition seems more effective in basic practice than in acid.—H. W. G.

MARKED ECONOMIES as well as slightly improved physical properties have recently been attained at several of the larger steel foundries, which specialize in railroad work, in the production of the high tensile pearlitic manganese steel for freight-car side frames and bolsters and similar castings. This steel, containing about 0.28 to 0.35 per cent carbon, 1.20 to 1.60 per cent manganese and usually small amounts of certain other alloys, is required to develop 90,000 to 100,000 lbs. per sq. in. tensile strength with good ductility and impact resistance, as normalized without liquid quenching. These properties are practically impossible to obtain in intermediate manganese cast steel without some other alloy addition. Lately it has been discovered that excellent physical properties are exhibited by normalized castings of this pearlitic manganese steel without any other alloy content if the steel is properly deoxidized with titanium.

The advantages of strong deoxidation of steel have been thoroughly discussed in recent years by Herty and others in numerous technical papers issued by the Bureau of Mines or published by the American Society for Metals or the American Institute of Mining and Metallurgical Engineers and these advantages may be listed briefly as including a higher grain-coarsening temperature or the maintenance of fine grain-size at higher heat-treating temperatures, the separation of more ferrite in the microstructure, and better impact resistance and ductility. Of course these effects are closely inter-related. Since with manganese above 1 per cent, steel tends to have a coarse grain, with less ferrite at usual cooling rates, and poor impact resistance and ductility, it is obvious that the advantages of thorough deoxidation are of even more importance in this kind of steel than in plain carbon steel with normal low manganese content.

But in cast steel the degree of deoxidation must be closely controlled for, if the steel is too strongly deoxidized, the sulphide inclusions are found to be arranged in a network pattern around the primary austenite crystals, with disastrous results on the ductility, in spite of any heat treatment. This effect of over-deoxidation was described by the writer in 1924 (*The Iron Age*, Vol. 114, page 1477) and in 1929 (*Trans.* A. S. S. T., Vol. 17, page 459), and was finally confirmed by Sims and Lilliequist (*Trans.* A. I. M. E., Vol. 100, 1932, page 154) in such a manner as to be generally realized and accepted by metallurgists today. By careful use of ferro-carbon-titanium, however, with good steel-melting practice, the advantages of strong deoxidation of pearlitic manganese steel have been obtained without the undesirable effect on the sulphide inclusions. The amount of ferro carbon-titanium which has been used most successfully in basic open-hearth practice is 5 lbs. per ton of charge.

Some representative physical properties of the newly developed manganese-titanium cast steel are given in the Table. These values were obtained without liquid quenching, the heat treatment consisting of a single normalizing from about 1600 deg. F., followed by a draw at about 1050 deg. F. The last treatment does not affect the microstructure, and probably not the properties either, but was used because it is believed to be useful for relieving strains in the large castings after normalizing.

Table I—Chemical and Physical Properties of Mn-Ti Steel

Heat No.	Chemical Analysis C	Mn	Si	P	S	Lbs. per Sq. In. Yield Point	Tensile Strength	Per Cent Elongation in 2 in.	Reduction of Area	Ft.-Lbs. Izod Impact
1	0.30	1.68	0.43	0.019	0.028	78000	106000	28.0	59.0	40.0
2	0.30	1.55	0.40	0.019	0.027	73500	99000	31.0	60.0	49.0
3	0.263	1.46	0.37	0.029	0.026	63000	91000	31.0	55.0	55.0
4	0.314	1.39	0.37	0.029	0.034	67000	96500	26.0	49.5	28.5
5	0.294	1.45	0.37	0.028	0.026	64500	97000	28.0	55.5	39.0
6	0.302	1.55	0.40	0.019	0.027	67500	94350	28.0	58.6	35.0
7	0.295	1.41	0.40	0.026	0.025	71850	97450	28.0	51.4	34.0

The first two heats in the Table were from a small induction furnace, but the others were made in 30-ton open-hearths; and all except No. 1 were treated with 5 lbs. of ferro carbon-titanium per ton, No. 1 having received only 3½ lbs. per ton. That these results are entirely acceptable for high-tensile pearlitic manganese steel may be appreciated by comparing them with the standard values for this grade of steel which are tabulated on Pages 404, 467, and 741 of the 1936 A. S. M. Handbook. The economy in using titanium in this steel at a cost of only about 40 to 50 cents per ton, instead of other more expensive alloys which have been used previously, is naturally desirable.

The heat treatment of this manganese-titanium steel does not require close control since it has been found that the grain does not coarsen in a reasonable length of time even at 1750 deg. F. It can be normalized therefore at any temperature from 1500 to 1750 deg. F. without any important change in properties.

TWO NEW APPLICATIONS OF

INDUCTION HEATING

by E. T. Cone

TWO NEW APPLICATIONS of induction heating are now being installed by the Ajax Electrothermic Corp., Trenton, N. J. The principal applications of this type of heating up to this time include electric melting in the Ajax Northrup high-frequency furnace, continuous heating of thin strip steel and tubes, drying or baking enamel on metal parts and the hardening of metal surfaces by quenching after induction heating as in the "Tocco" process of The Ohio Crankshaft Co., Cleveland, licensee of the Ajax Company.

The new applications referred to include:

1. Induction heating of tube ends prior to a series of forging operations.
2. Heating an end section of a large steel tube prior to a swaging operation.

In reference to the first of these new applications, Fig. 1 shows the individual heater control panel and the coil of the induction heating apparatus with two steel tubes inserted. High frequency power at 2000 cycles is applied to the coil and, in less than 1 min., 6 in. of the end sections of the two steel pipes are heated to 2200 deg. F. after which they are forged.

A special focus induction coil is shown in Fig. 2 revealing a narrow band at the end of a tube heated to 2200 deg. F. This is a subsequent operation to that described in the preceding paragraph. Fig. 3 shows a cross section of the focus one turn coil, the tube end, and indicates the sharply defined heating zone.

Fig. 1.—Individual Heater Control Panel and Coil for Inductive Heating of Tubes.

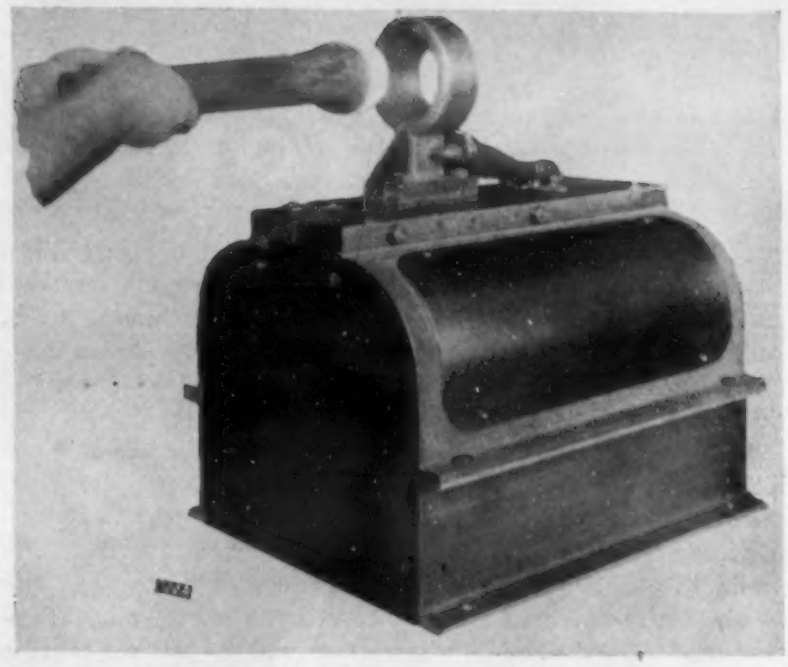


Fig. 2.—Special Focus Induction Coil Showing Narrow Band of a Tube Heated to 2200 deg. F. by Inductive Heat.

The Ajax Electrothermic Corp. states that, in connection with this device, the same fundamental type focus inductor coil is used as in so-called Tocco process for hardening crankshaft bearings, mentioned in the opening paragraph. This process was developed at Trenton and its refinements and automatic operation have been and are carried on by the Trenton company's sole licensee for the process applied to crankshafts and camshafts—The Ohio Crankshaft Co., which also has the sole right to sublicense the process for automotive parts and a restricted additional field. The Ajax Electro-

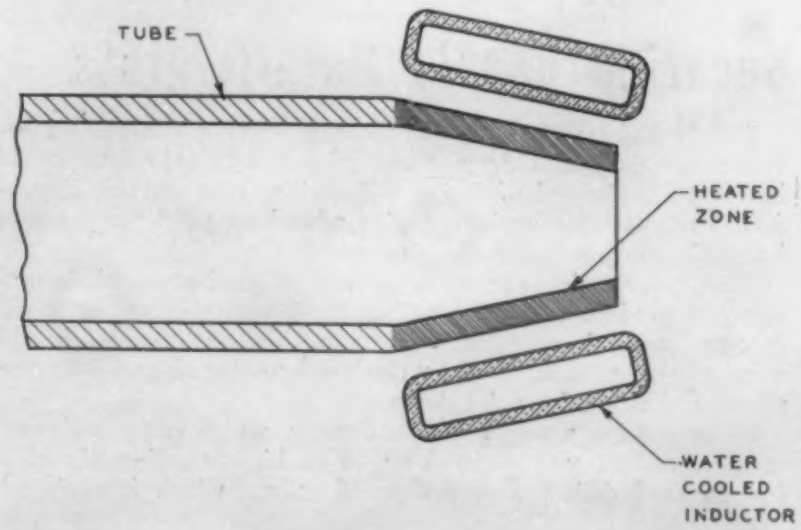


Fig. 3.—Cross Section of the Focus One Turn Coil Showing Heated Zone.

thermic Corp. markets equipment for surface hardening in all other fields.

The difference in the two applications is that, for surface hardening, a large amount of power is concentrated for a few seconds

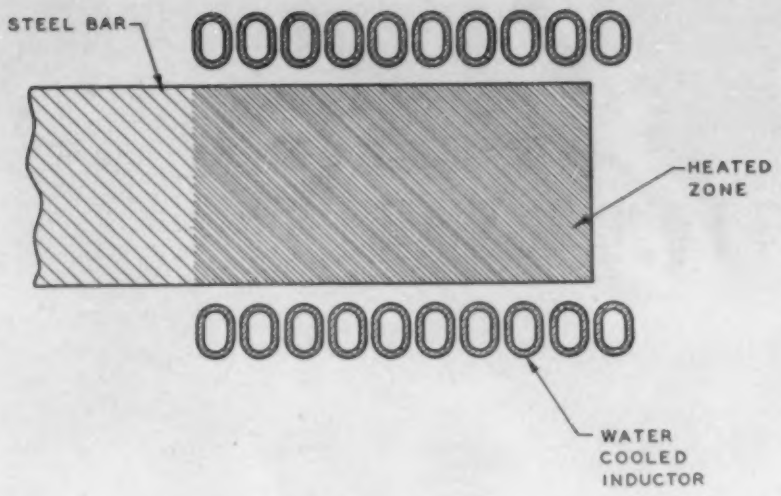


Fig. 4.—Cross Section Showing Uniform Heating of an End of a Bar or Billet.

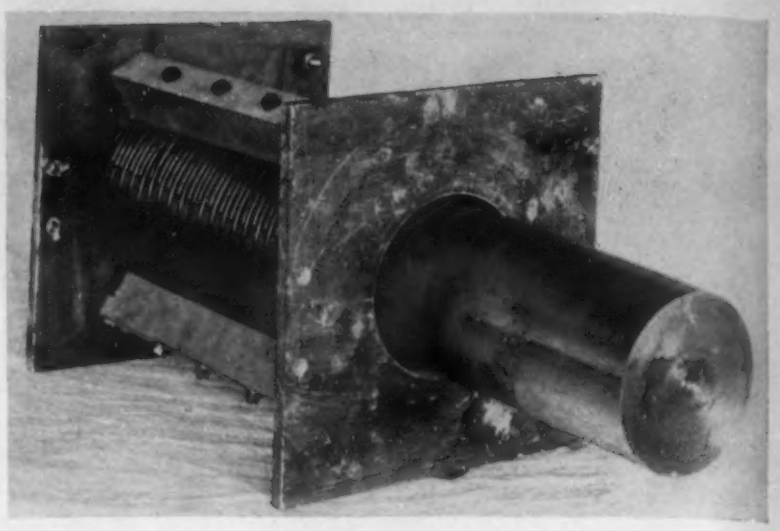


Fig. 5.—A Steel Tube Closed on the Unheated End—The Actual Set-Up Shown in Fig. 4.

so that the heating is entirely confined to the surface of the crankshaft bearing after which it is rapidly quenched to produce a very hard surface with a tough core. In the application for heating a tube end, Figs. 2 and 3, the power is not kept at such a high value; the time is extended to nearly a minute and the walls of the end of the tube are uniform in temperature at 2200 deg. F.

In Fig. 4 is shown the uniform heating of an end of a bar or billet, using this time a straight coil energized with high frequency current. It is pointed out as of interest that it is possible to heat uniformly the section of a 3-in. diameter billet to 2200 deg. F. in 2 min. A 7-in. square billet, tested in the Ajax plant, came uniformly throughout the section to 2200 deg. F. in 15 min. Temperatures were checked at the surface and at the center with thermocouples. To heat steel to a forging temperature requires about 400 kw.-hr. per ton overall.

The set-up described above is shown in Fig. 5. The same arrangement applies to the second new application mentioned in the first part of this article. Actually the piece of steel shown in Fig. 5 is a steel tube closed on the unheated end running about 5 in. in diameter with a ½-in. wall. To secure uniform temperatures in the wall section required about 1½ min.

Another point in this connection is that, for this installation, the Ajax Electrothermic Corp. is providing a graded temperature in the heated end of the tube. The open end (inside the coil) is heated to about 2000 deg. F. and gradually tapers back to 1800 deg. F. at the end of the 6½-in. heated section. This is regarded as ideal for forging operations and it is easily accomplished by altering the coil turns per inch or the location of the load in the coil. If, however, the user desires an end section at uniform temperature throughout with a sharply defined heated zone, this can be easily accomplished.

The method lends itself satisfactorily and nicely to automatic control and this is planned for both applications.

A LETTER TO THE EDITOR

Securing Usable Metallurgists

To the Editor: It occurs to me that a closer cooperation between metallurgical industries and educational institutions would benefit both. Instead of hiring technical men as you are able to find them, why not institute a plan whereby a yearly crop would be produced, grown according to specifications?

We all agree that one or more years of graduate work is necessary to produce a usable metallurgist. We also know that many concerns spend large sums in research. The graduate work and some of the research could be combined to the advantage of the school and the industrial concern.

My suggestion would be for a concern, which yearly adds one or more college men to its force, to establish a fellowship of a few hundred dollars at a designated college which is equipped to give the desired training; that one or two men of the graduating class be selected and put to work in the plant for the summer; after this observation period, that one of this number be sent back to college for one or more years of graduate work, to do research on a problem suggested by the company financing the fellowship.

At Vanderbilt University the chemistry department has been cooperating in this way for several years with one company. Their metallurgist states "they get men trained as they want them and that it saves them money."

I hope that you can find space to print this as an appeal to executives and technical directors.

W. P. FISHEL,
Assistant Professor of Metallurgy.

Vanderbilt University,
Nashville, Tenn.

A CHUCKLE

"Novel" Publicity

We note a head line in *The Iron Age,* April 8, 1937, page 105, "U. S. Steel develops Monel Rail Exhibit." From the text we gathered that the Editor meant "Novel," and he so stated in a correction in a later issue, but that the proof reader didn't correct it is a tribute to the Nickel company's publicity for its products.—H. W. G.

Metallurgical and Commerce News

BY THE EDITORS

Cast Crankshafts for Autos Instead of Forgings

The prevailing practice of most manufacturers of automobiles is to use forged steel crankshafts in their engines. There are a few, however, which are using cast iron or cast steel crankshafts. The cast steel crankshaft, developed and made by the Ford Motor Company, is outstanding. There are also some cast iron crankshafts made by the Campbell, Wyant & Cannon Foundry Co., North Muskegon, Mich., which are used by certain producers of automobile and Diesel engines.

The composition of the crankshafts referred to above is as follows in percentages:

	Ford	"Proferall x"	Caterpillar Tractor	"Frankite" *
Total Carbon..	1.35 to 1.60	2.40 to 2.80	2.95 to 3.05	2.75 and 3.00
Silicon	0.85 to 1.10	2.25 to 2.75	2.00 to 2.10	1.90 and 2.30
Sulphur		0.10 max.	0.06 to 0.08	0.08 max.
Phosphorus ...		0.15 max.	0.05 to 0.07	0.20 max.
Manganese ...	0.60 to 0.80	0.80 to 1.20	0.70 to 0.80	0.75 and 0.55
Nickel	.....	1.00 to 1.20	1.50 to 1.60	1.50 and 1.00
Molybdenum ..	.....	1.00 to 1.20	0.75 to 0.85	0.75 and 0.50
Copper	1.50 to 2.00	.....	.....	.....
Chromium ...	0.40 to 0.50	.....	.....	.....

* Two types.

The Ford crankshaft is a high carbon copper-chromium-silicon alloy which is heat treated to convert the white iron casting into a steel-like material. The "Proferall x" of the Campbell, Wyant & Cannon foundry, the two "Frankite's" of the Frank Foundries Company and the analysis used by the Caterpillar Tractor Company are all alloy cast irons, also heat-treatable.

In a paper—"Cast Camshafts and Crankshafts"—delivered by F. J. Walls, metallurgist, International Nickel Company, New York, recently at a meeting of the New England Section of the Society of Automobile Engineers, their various compositions were discussed.

Continuous Rolling of Hot Strip Steel

Continuous rolling of hot strip steel is no child's play, according to A. F. Giese, Jr., of the Carnegie-Illinois Coke Works, Gary, Ind.; in a paper on this subject before the recent general meeting of the Association of Iron and Steel Engineers at Youngstown. Mr. Giese clearly demonstrated that the difficulties involved in economically producing a first-class job have been seriously underrated.

Economical operation depends on careful choice of slab size, method and amount of heating and selection of hearth material. Chromeore, particularly in view of the improved performance obtained thereby, was strongly advocated as an economical hearth material in place of the customary materials. Poor surface, the bug-bear of the rolling-mill operator, may result from guide-marks, rolled-in scale, split centers and scale-laps caused by over-draft, worn or untrue rolls or failure to heat slabs to, or maintain them at, a sufficiently high temperature. Roll and spindle breakage can be prevented only by the most careful and gradual establishing of pass design, avoidance of over-draft, and provision of adequate water for the rolls.

Stainless Steels iu Germany

An order has been issued by the German Government authorities prohibiting the manufacture of certain articles from stainless steel for the domestic market. This report is on the authority of the United States Department of Commerce.

This is said to be the first restriction imposed on the use of these steels. The restriction is evidently aimed at those stainless steels which contain nickel because this metal is scarce in Germany and very difficult to obtain. This is explained partly by the fact that the restriction is imposed on the use of these steels in such products in which stainless steels have found new important outlets in recent years. It is stated that industrial apparatus and machines have been severely restricted in the use of stainless steels, especially brewery equipment, and machines and containers for the various foodstuffs industries.

Of decided interest is the statement that stainless steels containing chromium and manganese, but no nickel or not more than 1.50 per cent nickel, can be used until further notice except in certain products. The fact that a stainless steel in which at least a substantial portion of the nickel is replaced by manganese has been promoted to some extent in this country is of related interest. It is understood that such chromium-manganese-nickel steels are being quite extensively used now in Germany. Some authorities expect that the foreign interest will ultimately result in more energetic application of such alloys here, with the possible outcome of two classes of commercial austenitic stainless, the Ni-Cr and the Mn-Cr.

Importance of Cemented Carbides

In a recent broadcast over the network of the N. B. C., Dr. Zay Jeffries, one of the leading metallurgists of the country, discussed "Cemented Carbide." Dr. Jeffries is chairman of the board of the Carboloy Company, Inc., Detroit, and a consulting metallurgist for the Aluminum Company of America.

After discussing the general properties and the manufacture and uses of brands—"Carboloy," "Vascoloy-Ramet," "Firthite," "Teco," "Cutanit" and "Widia," he closed by outlining the chief points in the importance of such carbides as follows:

1.—They are revolutionizing the machine tool industry; rugged machines with higher speeds and greater horsepower, are being provided to take advantage of their properties.

2.—The user of an automobile has brake drums and clutch fans of harder metal than could be economically machined without cemented carbide.

3. New alloys, heretofore commercially unmachinable, have been put on the market.

4.—Dimensional tolerances of machined parts and drawn products have been narrowed, resulting in improved machines and greater flexibility in the interchangeability of parts.

5.—By substituting cemented carbide for other materials and operating at higher speeds, the output per shift of a great variety of machines has been markedly increased.

This lusty child of the metal industry, said Dr. Jeffries, is destined to have great economic and social consequences, though it is only in its early stages of development.

Cast Instead of Forged Camshafts

Although the forged steel camshaft is being and has been used for some years by automobile builders, the cast iron camshaft is now being extensively used. The practice of the Ford Motor Company is an example of the cast iron camshaft. Besides this, there are large quantities of camshafts of cast iron being made by the large foundry of Campbell, Wyant & Cannon, which are used by various automobile manufacturers.

The average composition of the Ford and the other cast iron camshaft, known as 'Proferall,' is as follows in percentages:

	Ford	"Proferall"
Total Carbon	3.30 to 3.65	3.10 to 3.40
Silicon	0.45 to 0.55	2.10 to 2.40
Sulphur		0.10 max.
Phosphorus		0.20 max.
Manganese	0.15 to 0.35	0.50 to 0.75
Chromium	0.00 to 0.25	0.75 to 1.00
Nickel		0.20 to 0.40
Molybdenum		0.40 to 0.60
Copper	2.50 to 3.00	

Both of these types are alloy cast irons or high test irons and are capable of heat treatment. Manifestly the Ford composition is the cheaper to produce. These analyses are from a paper—"Cast Camshafts and Crankshafts" by Fred J. Walls, metallurgist, International Nickel Company, New York, which he delivered recently before the New England Section of the Society of Automobile Engineers in Boston.

Demand for Foreign Spiegeleisen Expands

Demand for foreign spiegeleisen has expanded recently to such an extent that the imports for the last two years exceed those of any years for some time.

The following table, compiled from Government statistics, furnishes a record of the imports of spiegeleisen since 1929 inclusive —in gross tons:

Year	Total Imports	Tons per Month
1929	13,828	1,152
1930	13,406	1,117
1932	8,364	700
1933	26,277	2,190
1934	21,234	1,770
1935	32,375	2,700
1936	52,018	4,335
1937 (2 mos.)	1,890	945

With the imports at 4,335 tons per month in 1936 (and 2,700 tons monthly in 1935) there is revealed the magnitude of this movement. In the boom year of 1929 these imports were only 1,150 tons each month. There has been a decided expansion since 1933.

While the American production of spiegeleisen bulks large, the imports are becoming more of a factor in total consumption.

Germans Develop Alloys of Zn to Save Cu, Pb and Ni

To save imported copper, lead and nickel, the German zinc industry has made important contributions. Because zinc is about the only metal produced entirely from domestic ores, it is being used extensively by the Germans in a number of alloys to replace brass and bronze.

According to Foreign Metals and Minerals, published by the Department of Commerce, Washington, the most important of the new alloys, is one known as "Giesche ZL2" with 4 per cent Al and 1 to 1.50 per cent Cu. It is being used in place of bronze, red brass and cast brass. It may be die-cast or cast in sand or iron molds.

Another alloy is called "Giesche ZL3" with 4 per cent Al and 0.5 per cent Cu. It lends itself to pressing and drawing, and corresponds in its properties to rolled brass.

Experiments are under way on a number of other zinc alloys.

Very Heavy Output of Ferromanganese

With the sharp upturn in steel production this year, there has come a decided increase in the output of ferromanganese by American blast furnaces. The first quarter total has been 75,045 gross tons or 25,015 tons per month. Compared with 1936 and with previous years the authoritative record is as follows in gross tons:

Year	Total Output	Tons per Month
1913	119,493	9,960
1918 (war)	333,027	27,750
1929	335,799	27,820
1930	276,500	23,040
1931	212,115	17,673
1932	57,342	4,780
1933	136,852	11,400
1934	124,190	10,350
1935	185,173	15,431
1936	254,728	21,227
1937 (3 mos.)	75,045	25,015

Thus at over 25,000 tons per month this year to April, the ferromanganese production is 22.5 per cent higher than in 1936. It is substantially in excess of the volume in 1930 of 23,040 tons each month and is nearly six times the volume of only 4,780 tons monthly at the low point of the depression in 1932. It is not far from the record American production of 27,820 tons per month in 1929.

That the output of this important steel making alloy is a measure of the rate of steel ingot output is clearly demonstrated by these data. The ferromanganese production is a barometer of the trend of the American steel industry.

Very Heavy Manganese Ore Imports

Imports of manganese ore in 1936 almost established a new record—they approached very close to the record imports of 1926. According to official Government data the manganese ore imports —ore containing approximately 50 per cent manganese and known as metallurgical ore—the record for 1936, compared to a period of years, is as follows in gross tons, including January 1937:

Year	Total Imports	Tons per Month
1925	610,131	50,840
1926	708,400	59,000
1927	617,700	51,400
1928	419,600	34,900
1929	648,800	54,000
1930	562,600	46,900
1931	490,600	40,885
1932	110,634	9,220
1933	288,187	26,015
1934	341,338	28,445
1935	383,500	31,960
1936	706,607	58,800
1937 (2 mos.)	52,583	26,290

Thus at 58,500 tons per month for 1936, the imports just fell short of the record of 59,000 tons monthly in 1926 and exceeded by a considerable margin the 1929 imports of 54,000 tons each month.

With the returns for only two months of 1937 available, the rate this year is small but this will probably be increased by the inflow in later months.

The extent of the recovery in the steel industry since the bottom of the depression in 1932 is reflected by these imports—an expansion from only 9,220 tons per month in 1932 to 58,800 tons in 1936 or an increase of over six fold. As the steel ingot production expands, the imports of ore for the production of ferromanganese must also increase.

HEARTH REFRACTORIES

FOR STEEL MAKING

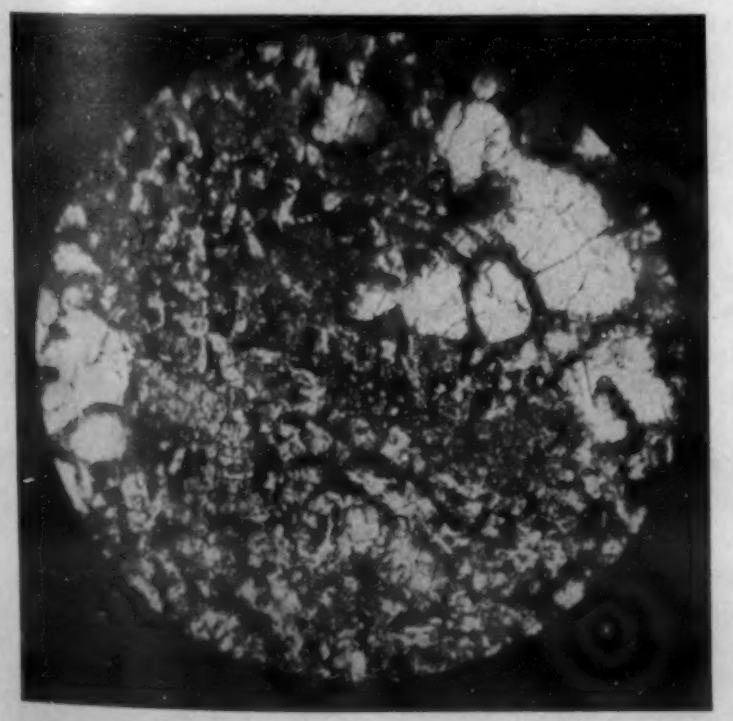
by W. J. MacCaughey and H. C. Lee

Department of Mineralogy, Ohio State University, Columbus, and Research Department, Basic Dolomite, Inc., Cleveland, Respectively.

STEEL MAKING CONSISTS IN GENERAL of the controlled elimination of certain metalloids such as carbon, phosphorus, silicon, manganese, sulphur, etc. The successful accomplishment of this objective is assured only by the careful control of the many variable factors of furnace operation, an important one being the composition and maturity of the slag formed in the process. The slag serves as a medium to store up the so-called impurities removed from the metal by oxidation, and to prevent their reversion once they have been removed.

In the steel making process, two immiscible liquids are formed. One, the metal bath; the other, the slag. The slag is an oxidized system molten for the most part and containing in solution the products of oxidation and fluxing formed in the refining of the steel. Part of the slag may, however, be undissolved and carried in suspension. That part of the slag which is suspended rather than dissolved may comprise residual fluxes which have not completely reacted, particles of the hearth refractory loosened in the refining process, and in the case of basic open-hearth slags, dicalcium silicate not yet dissolved.

Fig. 1—Open-Hearth Slag—Photomicrograph, Thin Section, Magnification 100 X. Tapping slag, immature, showing unfluxed, undissolved dicalcium silicate as large white grains.

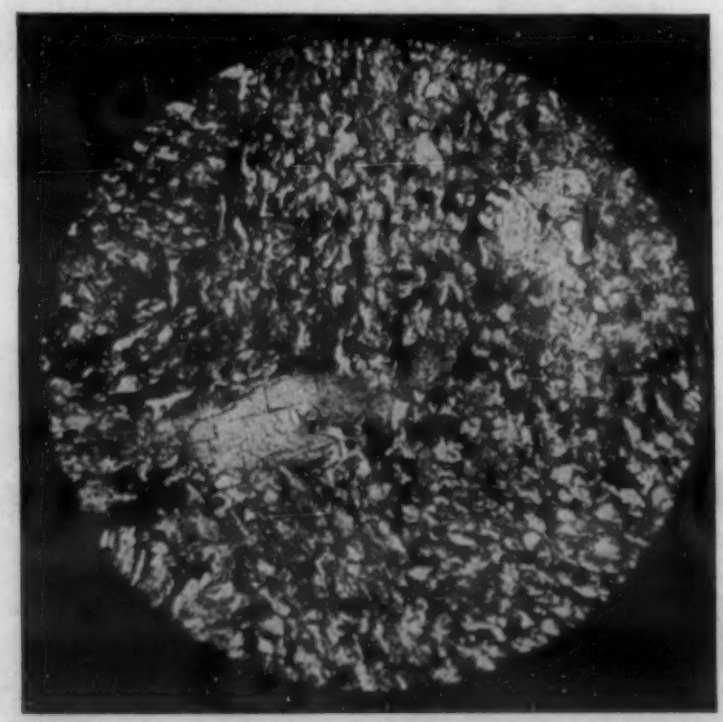


The molten bath of steel has dissolved in it carbon and silicon, and oxides of iron and manganese. As the heat progresses, the amount of dissolved carbon becomes less while the amount of iron oxide increases. The change in the metalloid and oxide content of the bath is accompanied by changes in composition of the slag.

Two Types of Steel Making

The steel making processes may be classified into two divisions, depending upon the type of slag that is produced. In the acid type of steel making, the slags formed are high in silica and relatively poor in basic oxides. To this division belong the acid open-hearth process and the Bessemer process as it is practiced in this country. The hearth refractory used in the acid processes is of a high silica composition, and the hearth materials contribute to the formation of this slag. The basic oxides found in the slag are al-

Fig. 2—Open Hearth Slag—Photomicrograph, Thin Section, Magnification 100 X. Tapping slag, well digested slag dicalcium silicate in solution, large grains of undissolved lime showing cubic cleavage.



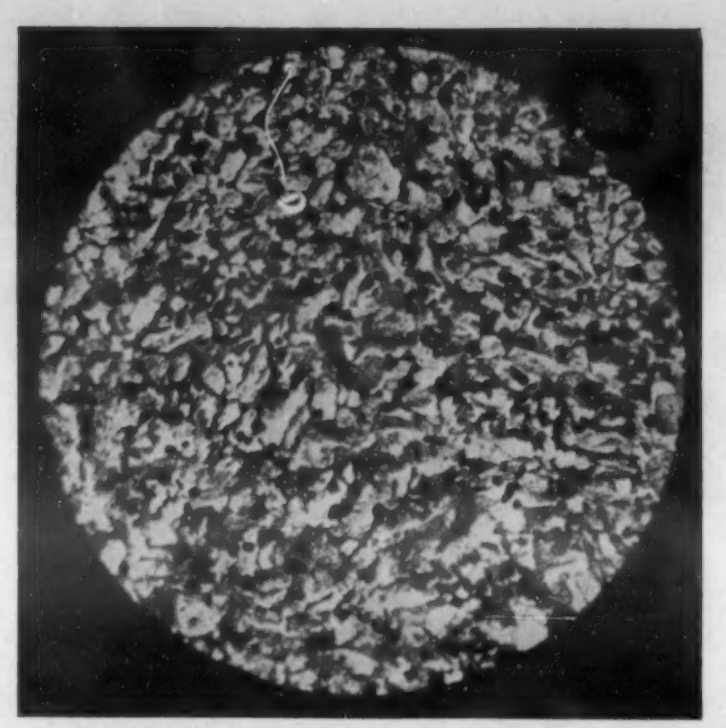


Fig. 3—Open Hearth Slag—Photomicrograph, Thin Section, Magnification 100 X. Tapping slag, well digested, dicalcium silicate and lime in solution.

most completely oxidation products of the metal being refined.

The basic open-hearth process is of more general application in this country, and over 80 per cent of the tonnage of steel made is basic open-hearth. The basic open-hearth process has many advantages over other processes, but its outstanding success is largely due to the fact that phosphorus can be more successfully removed by the use of a basic slag, that is, a slag which is fairly rich in lime and low in silica. The slags formed in this process, in spite of a highly basic composition, build up in iron oxide content as the heat progresses and as the carbon content of the metal bath decreases. In low carbon heats, the iron oxide content of the slags may even run over 40 per cent.

Fig. 4—Open Hearth Slag—Photomicrograph, Thin Section, Magnification 100 X. Same tapping slag as Fig. 3 in polarized light, crossed nicols, dicalcium silicate crystallizing from solution with oxide phases to form mosaic intergrowths.

The slag formed in the steel refining process is generally more corrosive on the refractory hearth than is the metal itself. For this reason, the type of hearth material used in steel making is dictated primarily by the type of slag formed.

The successful application of the basic open-hearth process by Thomas and Gilchrist depended upon the development of a refractory hearth that would resist the corrosive effect of the iron oxide dissolved in the basic slag. They found that basic refractory materials rich in magnesium oxide were particularly resistant to iron-rich slags, and in the early development of the basic process, both dolomite and magnesite, calcined in both cases, were separately used for hearth material.

Calcined magnesite contains as its essential constituent magnesium oxide, which, when crystallized, is known as the mineral periclase. For a long period of time, Austrian magnesite was the standard refractory material for basic open-hearth practice. The Austrian magnesite contains as an accessory constituent, iron oxide which makes it particularly suitable for open-hearth material. When iron-free magnesites were used, it was found necessary to clinker these magnesites by the addition of certain fluxes such as iron oxide, aluminum oxide, and silica.

Dolomite as a Hearth Refractory

The shortage of magnesite during the World War led to the widespread use of dolomite as a refractory, particularly dolomite that was clinkered at a high temperature and with the introduction of additional fluxes not already present in the dolomite. Such clinkered dolomite refractories reached a high state of development and they were found to be particularly valuable in the patching or repairing of basic hearths, though magnesite was still used to build new hearths. Clinkered dolomites displaced magnesite as a patching material, partly for economic reasons but largely because of the readiness with which clinkered dolomites fused into the furnace and became a part of the refractory hearth.

Clinkered dolomite contains somewhat less than 40 per cent MgO and more than 50 per cent CaO. Since lime is an active flux in the open-hearth process, it would not seem reasonable to expect that this lime would remain as a permanent part of the refractory hearth, but that it would gradually be eliminated in the fluxing process. In spite of this lack of permanence of dolomite, its use as a patching material became almost universal due to the rapidity with which satisfactory repairs could be made.

The principal objection to the use of magnesite was the long time required to set and incorporate it as a part of the hearth. For major repairs, it was customary to mix the magnesite with a certain amount of slag. On account of its slow coalescence, there was danger, if this patching was not satisfactorily performed, that the patch might float out of the hole in which it had been placed. Many steel men thought that there was a need for a magnesite with a high magnesia content which had the quick coalescing properties of clinkered dolomite.

Periclase as a Hearth Refractory

Magnesia, in the form of periclase, offers peculiar advantages for use in basic open-hearth steel furnaces. It has a melting temperature of 2800 deg. C., (5072 deg. F.),

the highest melting temperature of the common refractory oxides. It has a specific gravity of over 3.6, which should help resist the floating action of the metal bath. Its hardness of six, equal to cold steel, would enable it to resist abrasion. Its most valuable properties, however, are chemical. It has a low solubility in basic open-hearth slags, and it possesses the property of absorbing several times its own weight of iron oxide without seriously impairing its use as a refractory. At the high temperature of the open-hearth, magnesite refractories do not possess great strength, largely because of a gradual softening of the bond which holds the magnesium oxide particles together. This softening of the bond, however, if controlled, is not harmful in the hearth of a furnace, but on the other hand produces a valuable thermo-plastic property in the refractory which enables it to become knitted into a single unit and permits the incorporation of the magnesite or dolomite as a patching material when holes develop in the refractory.

Cracks formed in the basic magnesia hearth by cooling the furnace to room temperatures, as in the replacement of a roof, are closed in reheating by virtue of the thermo-plastic nature of the magnesite refractory. In high magnesia refractories, the magnesia is generally present in the form of rounded pea-like bodies of microscopic dimensions. These periclase grains do not seem to have the ability to develop into larger particles to form more coarsely crystalline structures. This habit of forming aggregates of rounded periclase grains instead of large interlocking crystals is peculiar to high magnesia refractories as matured in steel furnaces. This type of structure requires the presence of an auxiliary bond and in general the structure of basic magnesia bottoms is one of periclase grains cemented together by other minerals which at operating temperatures may in part form a liquid.

Importance of Interstitial Bond

It would seem, therefore, that an important part of a high magnesia refractory should be the amount and character of the interstitial bond that holds the periclase grains together and serves to knit the refractory readily into the basic hearth of the furnace. Such a bond should also develop maximum shrinkage in the basic refractory material before the latter is applied to the furnace hearth. It should be present in a small amount, thereby insuring only small subsequent changes taking place in the furnace. The bond should be of such a nature as to impart to the high magnesia refractory the rapid coalescence of clinkered dolomite. Furthermore, the bond should be in chemical equilibrium with magnesia, the principal constituent of the high magnesia refractories, and be in equilibrium with the slag developed in the furnace.

This bond should be present in sufficient quantity to adequately coalesce the refractory into place and any excess should be avoided. The bond should be of such a character that it will not materially increase in amount as the heat progresses. While a slight pyroplastic condition is desirable in forming a dense, monolithic structure, an excess of bond or the formation of an excessive amount of liquid as the heat progresses produces a bottom which is easily eroded. Careful petrographic investigations of basic hearths and basic refractories, together with equilibrium studies, were made to determine the effect and permanence of suitable bonds.

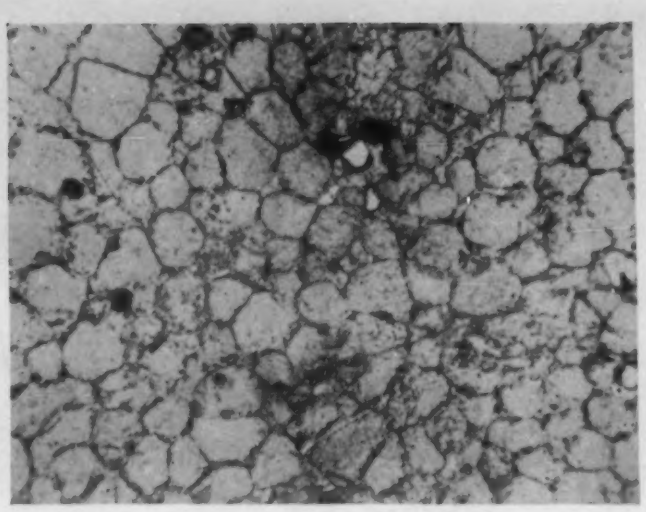


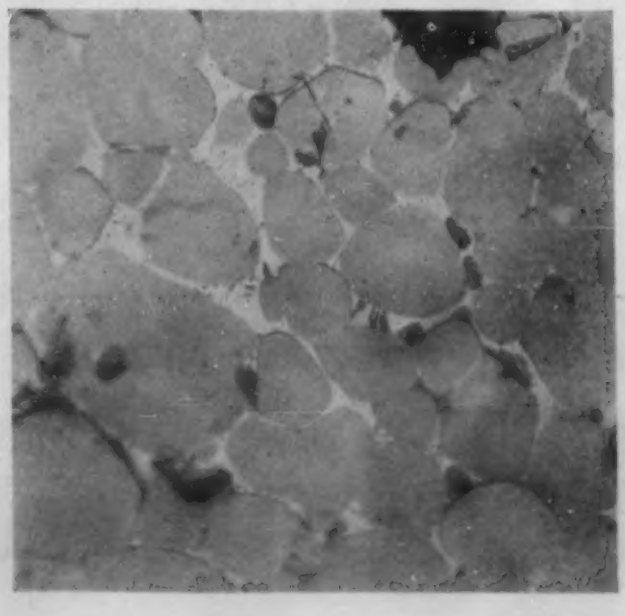
Fig. 5—Open Hearth Bottom—Photomicrograph, Thin Section, Magnification 100 X. Basic bottom showing essentially periclase. Bottom originally put in with magnesite containing 16 per cent lime and 6 per cent silica, showing concentration towards MgO in service.

Calcium Ferrite as a Bond

Lime combines with ferric oxide to form compounds known as calcium ferrites, which have low melting temperatures and are in equilibrium with magnesium oxide. Calcium ferrite possesses certain advantages as a bond for magnesia refractories. Its low melting temperature and the readiness with which it wets periclase make a small amount of bond possible. Calcium ferrite serves as a mineralizer to shrink the refractory into hard, dense particles during the manufacturing process and later functions as a bonding agent to coalesce the magnesia particles into a dense, monolithic hearth.

Substitution of alumina for some of the iron oxide in the calcium ferrites is possible without changing materially the melting characteristics of the bonding material. It has been found that a calcium ferrite-bonded high-magnesia refractory has the rapid coalescence of a clinkered dolomite and for that reason it is not necessary to mix open-hearth slag with the high magnesia refractory as has previously been necessary with magnesite refractories. By using a calcium ferrite bond in a high magnesia refractory, a rapid

Fig. 6—Thomasite—Photomicrograph, Polished Section, Reflected Light, Magnification 350 X. Thomasite refractory: Large spherical grains, periclase; light-colored, interstitial phase, calcium ferrite; small, dark grains, dicalcium silicate imbedded in calcium ferrite.



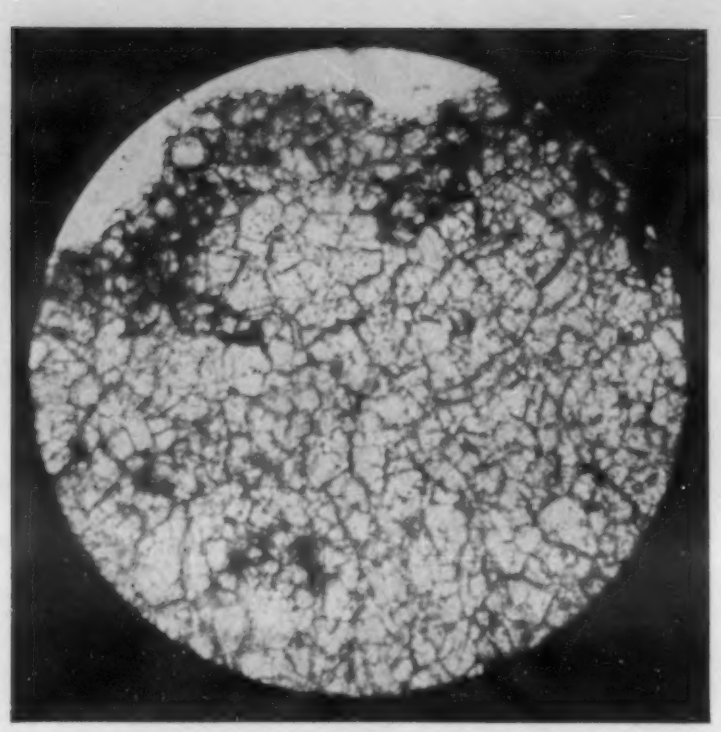


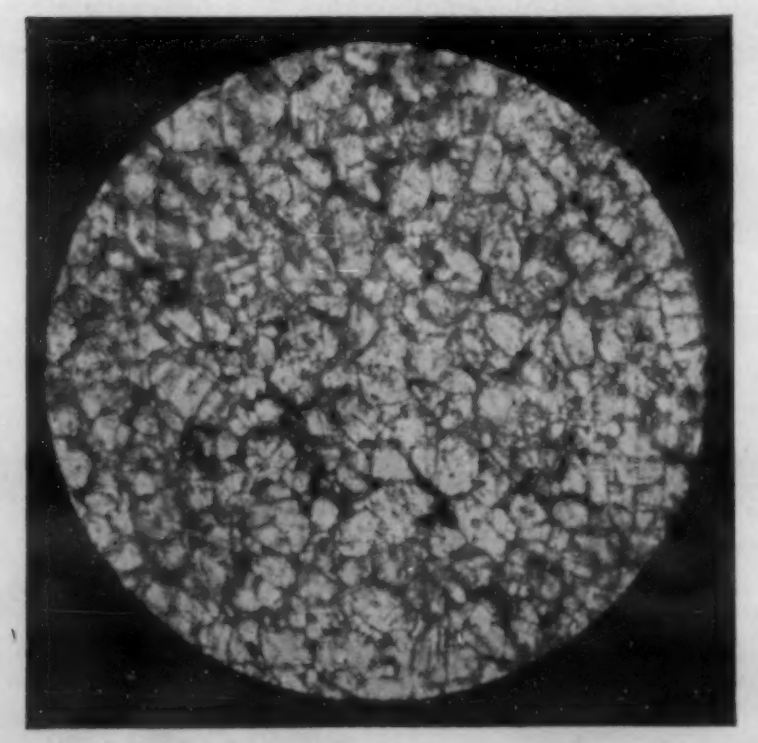
Fig. 7—Thomasite—Photomicrograph, Thin Section, Magnification 100 X. Thomasite refractory showing calcium ferrite concentrated at edge of grain; light colored mineral, periclase.

coalescing action is provided, thus minimizing the refractory dilution usually obtained from slag additions. The calcium ferrite bond has the further advantage that, when placed in the open-hearth bottom and in contact with the metal bath, the calcium ferrite is partly reduced and the low temperature bond is converted into a more refractory phase, which serves to harden the refractory or dry it up.

In order to insure the development of a calcium ferrite bond, it is necessary to keep the silica content of the magnesia refractory low. Lime combines preferentially with silica to form calcium silicate before it is available to form calcium ferrite with ferric oxide.

A serious limitation on designing a satisfactory bond for high magnesia refractories lies in the associated mineral impurities ordinarily found with magnesite. Serpentine, a commonly associated impurity, is a hydrated magnesium silicate, and acts as a diluent in the refractory. Furthermore, magnesium silicate is not stable in contact with open-hearth slags, and, therefore, not a permanent part of the refractory.

Fig. 8—Thomasite—Photomicrograph, Thin Section, Magnification 200 X. Thomasite refractory, interior of grain; light colored mineral, periclase; dark, interstitial phase, calcium ferrite.



Some Difficulties Encountered

In attempting to prepare a magnesia refractory bonded with calcium ferrite, difficulty was encountered in obtaining a suitable source of magnesite which would contain only a small amount of silica in the calcined product. The silica requires, as was said before, an additional amount of lime to be added to the refractory to convert the magnesium silicate (serpentine) into dicalcium silicate before any ferrite bond is developed. The necessity of adding 2 lbs. of lime to neutralize 1 lb. of silica before developing the ferrite bond made it desirable to seek a source of pure magnesite or its equivalent. It was thought possible to beneficiate the dolomites of northwestern Ohio by removing most of the lime. Since these dolomites contain only very small amounts of silica, this would furnish a suitable supply of pure magnesia.

During the development of such a process, a deposit of brucite (magnesium hydroxide) was found in Nevada. The brucite in Nevada occurs in massive deposits and is remarkably free from siliceous impurities, or the impurities are in such coarse fragments that they are easily removed in the mining operation. The availability of such a deposit of high magnesia, low silica mineral made it desirable to use such a mineral deposit before a magnesia separation process based on dolomite was completely reduced to commercial practice. Brucite, when calcined, yields magnesium oxide which is particularly suitable for the commercial development of a calcium ferrite-bonded magnesia refractory.

The manufacture of a calcium ferrite clinker calls not only for a source of low-silica magnesia, but also for careful proportioning of the lime with respect to the silica and iron oxide, and careful furnace control to insure the formation of calcium ferrite.

A Magnesia Refractory, Bonded with Calcium Ferrite

With careful control of raw materials and firing, a calcium ferrite-bonded, high-magnesia refractory was made of the following composition.

	Per cent
SiO_2	2.5
Fe_2O_3	7.0
Al_2O_3	1.0
CaO	10.0
MgO	79.5

The calcium ferrite developed in the above refractory produces hard, dense, refractory granules having a bulk density of 125 to 135 lbs. per cu. ft., and a true specific gravity of about 3.6.

Mineralogically, such a refractory consists of about 79 per cent periclase, 13 per cent calcium ferrite, and 8 per cent calcium silicate. At furnace temperature, the calcium ferrite fluxes part of the calcium silicate, producing some 16 per cent of bond. Sufficient calcium ferrite is formed to rapidly set the refractory in the furnace. However, the amount of both calcium ferrite and calcium silicate is maintained as low as possible in order to avoid refractory dilution. Magnesia is kept as high as possible to provide a maximum amount of periclase which gives permanence to the refractory and resistance to iron-rich slags.

The high density of the refractory and the ability of the refractory to coalesce produce a dense monolithic hearth of high magnesia content having a maximum resistance to iron-rich slags, which is so necessary with low carbon steels.

Practical Service Tests

Based on these principles, a carload of this high-magnesia, calcium-ferrite-bonded refractory was manufactured and a trial undertaken on a 150-ton furnace at one of the large steel companies. Objections on the part of the melter to using this new refractory, "Thomasite," without slag admixture had to be overcome. To remove the prejudice of the melter against applying the refractory without slag, two test samples were run on the breast of the furnace on top of raw dolomite, one with slag, and the other without slag. The sample without slag knitted together to form a solid cake over the mound of raw dolomite. One of the rods used for shaking down a heat was placed over the refractory and when the refractory was pulled out of the furnace afterwards, a clear impression of the rod was seen in the solid refractory cake. After this demonstration, the melter used the material as recommended and without slag admixture. The calcium ferrite-bonded magnesite was used over a period of days on the one furnace with satisfactory results.

During the test, a bad hole developed in one of the adjacent furnaces. This hole was of such large proportions that ordinarily magnesite would have been used for patching and considerable time spent on putting in the patch. At the suggestion of the melter, this hole was repaired with several layers of the new material, and patching accomplished in a short time. The patch was very satisfactory and withstood regular furnace operation during the week that the trials were run.

To distinguish it from other basic refractories, the high-magnesia ferrite-bonded refractory was given the name Thomasite in honor of the man who developed both the basic process and also the refractories that made it possible.

Editorial

(Continued from page A 37)

shadowed to some extent by the fact that, in the production of sheet steel for deep drawing, careful regulation of the quantity of copper and tin is already standard practice by some producers. Each heat is analyzed for copper and tin before tapping, because too much of these two elements in the steel renders the product unfit for deep drawing. One company keeps the copper under 0.06 per cent in all heats for such products.

As to the presence of chromium and vanadium, these do not, and may not, cause much trouble in the future because in the melting and refining process they largely disappear in the slags. On the other hand, nickel and molybdenum are more persistent and remain more completely in the steel. When these accumulate in larger proportions, possibly the more careful watching of the heats will be necessary when certain grades of steel are called for in which their presence in sufficient quantity might be prejudicial. Regulation of scrap by careful sorting is rapidly becoming an impossibility.

There is another angle to this situation, though. There is no agreement among different operators as to just what impurities, combinations, or amounts, actually exert discernable influence on the properties of the finished steel.

Each operator has a tendency to set up a hard and fast impurity specification on the basis of experience, with so many variables entering into that experience that proof of the effect of any one is not very clear. The divergence of opinion and resultant specifications for impurities is sufficient evidence that opinion, rather than demonstrable facts, is the basis.

Since this problem affects the whole steel industry, the steel industry as a whole might well foster an investigation to bring out the real facts.—E. F. C. and H. W. G.

Progress in Powder Metallurgy

That the development of powder metallurgy has progressed very rapidly in quite recent years was emphasized by a statement by Charles Hardy, president of Charles Hardy, Inc., New York—an authority in this field—that at present the consumption of powdered metals in the United States amounts to at least 6,000,000 pounds annually. This fact was brought out at a meeting of the New York Chapter of the American Society for Metals at which the evening's topic was Powder Metallurgy. The subject was ably presented by Gregory Comstock of Handy & Harmon, Bridgeport, Conn., also an authority.

Most metallurgists are familiar with some of the principles involved, but Mr. Comstock showed that this rather complex industry is largely in its infancy and that the prospects of its broadening use are excellent and impressive. He emphasized what he regarded as a distinguishing characteristic—that when powdered metals are mixed to produce alloys, and it is usually alloys that are thus made, the product obtained by pressing the mixed metals and then sintering, has all the properties, or an average of all of them, of the component metals. He contrasted this with fusion metallurgy where many of the inherent properties of the metals involved are changed by melting. The fact that certain products or shapes can be made of alloys by powder metallurgy which cannot be produced by melting and pouring is an advantage, he said, citing tungsten carbide and similar tools.

It was also pointed out that success in powder metallurgy depends to no small extent on the size and shape of the particles which is also dependent on the method of preparation—by reducing the oxides, by electrolytic deposition, by chemical precipitation, or by grinding. Powdered metals made by electrolysis are dendritic in shape and more easily adhere to each other.

This highly interesting subject, which may be classed as diffusion in solid metals, is a broad one and one in which the research at present applied will bring out new facts and new products.—E.F.C.

Courtesy: Holcroft & Co., Detroit

Charging End of a Controlled Atmosphere
Gas Carburizing Furnace for Gears

AN EXPERIMENTAL STUDY OF

Gases for Controlled Atmospheres—I

IN THE HEAT TREATMENT OF STEEL

by E. E. Slowter and B. W. Gonser

Chemical Engineer and Metallurgist, Respectively, Battelle Memorial Institute, Columbus, O.

THE EXTENSIVE COMMERCIAL USE of controlled atmospheres in the annealing and normalizing of low carbon steel has brought increased attention to the problem of similarly protecting higher carbon steels, especially prior to quenching, in what is termed "bright hardening." The usual cheap atmosphere produced by burning some fuel gas with a deficiency of air for the bright annealing of low carbon steels is required only to give bright, untarnished work. In bright hardening, appearance is not so important, but it is necessary that the atmosphere be neither decarburizing or carburizing to the medium and high carbon steels.

The urge for bright hardening comes from the desire to avoid high finishing costs after heat treatment. Loss of material and change in dimensions by scaling and pickling or finish grinding are certainly worth avoiding if this can be economically accomplished. The handling of finished forgings, carbon steel tools, dies, springs, and the like, would be obviously facilitated if there were no surface attack during the hardening treatment. A soft, decarburized skin, however, is to be avoided just as carefully as a scaled surface. Indeed, it is generally considered to be the lesser of two evils to have a thin scale rather than a thin decarburized layer. Sometimes the two accompany each other, but it is possible to avoid decarburization by allowing enough scale to form. A thin adherent scale may be harder to remove by pickling than a thicker one that flakes off more readily, hence half-way measures of protection may be worse than none at all.

Some protective gases, at present used in bright hardening, are so regulated that an extremely thin skin, intentionally carburized, is produced on the surface. Another means is to use the vapor of cracked oil as in actual carburizing procedure. This is possible since the shorter time and lower temperature of heating for quenching, compared to actual carburizing conditions, gives a comparatively mild carburizing effect. Some hardening is also being done in cracked methanol vapor.

TYPES OF GASES FOR CONTROLLED ATMOSPHERES

Partly Burned Gases

Commercial controlled atmospheres for bright annealing and normalizing are commonly prepared by burning with a deficiency of air such fuel gases as natural gas, propane, butane, and city gas. Momentarily leaving out of the question the moisture from burning some of the hydrogen (already present in city gas and produced in the others by cracking of hydrocarbons) the composition of the resultant gas varies with the fuel, the gas-air ratio, and conditions under which it is burned.

Some typical ranges of the gases produced are shown in Fig. 1 from Marshall[1] for Schenectady city gas, Fig. 2 from Heyn[2] for Toledo Natural gas, Fig. 3-A from Krogh[3] for Providence city gas and Fig. 3-B for Pyrofax (99% propane, C_3H_8). Fisher[13] has recently shown curves for several other fuel gases. The gas composition is always controlled by gages which show the proportions of gas and air being supplied. Krogh also suggests measurement of the thermal conductivity of the gas, a function primarily of the hydrogen content. It will be noted from the figures that a slight change in the air:gas ratio may materially alter the composition of the gas produced. Common ratios are $2\frac{1}{2}$ to 3 parts of air to 1 part city gas, 6 parts air to 1 part natural gas, and 11 or 12 parts air to 1 part propane. Omitting the presence of moisture, the compositions of such gases and their partially burned products are shown in Table I.

An atmosphere made from city gas will contain some 18

Installation of 40 Vertical Tube Furnaces Having a Capacity for Annealing 350,000 Tons of Tin Plate per Year in a Controlled Atmosphere. (Courtesy: Lee Wilson Engineering Co., Cleveland)

to 20 per cent water vapor; that from natural gas perhaps 10 per cent or more. Some commercial furnaces lead the fuel gas and air directly into some part of the furnace chamber, hence this 10 to 20 per cent steam surrounds the work along with the CO, CO_2, H_2, CH_4, N_2 mixture. In general practice, however, the partly burned gas is cooled in a water cooler or by a water spray to nearly room temperature. This eliminates much of the moisture but it is still saturated at the temperature to which the gas is cooled, This may be from 1 to 2 per cent water vapor, i.e., chilled to 45 and 65 deg. F. respectively. To eliminate additional moisture, refrigeration is often used, and the cooled or chilled gas is sometimes further dehydrated by passage over silica gel or activated alumina which removes all but traces of moisture.

Dry Gas Producers

In order to make moisture-free gas, a "dry gas producer" using relatively pure carbon, such as charcoal or a special coke, may be employed. This should give a simple gas, high in CO, since, if all the oxygen of the incoming air were changed to CO by combining with pure carbon at a sufficiently high temperature, the gas would contain 34 per cent CO, 66 per cent N_2. Under commercial conditions, however, such gases actually contain small amounts of CO_2 and H_2. Hydrogen is formed if the air is fed to the producer, and the coke or charcoal are not made perfectly dry, since any moisture will react with the hot carbon to give CO and H_2. This hydrogen may react to some extent to form CH_4. According to Cone[5] these commercial gases will contain 28-31 per cent CO, 0.5 to 3 per cent CO_2, 0.5 to 1.5 per cent H_2 and perhaps a fraction of a per cent of CH_4.

Tamele[6] recommends charcoal generator gas for bright annealing and for use in the white burning of porcelain ware. Gould and Toole[7] found up to 4 per cent H_2 in a

Table I.—Typical Commercial Partially Burned Gases for Furnace Atmospheres Used in Heat Treatment of Steel

SOURCE	H_2	CO	CO_2	$CH_4 + C_2H_6$	O_2	N_2
Marshall, Schenectady city gas	54.2	7.0	1 8	30.4	1.6	5.1
Burned 2.8 air: 1 gas ratio	10.3	7.6	4.5	1.3	...	Balance
Krogh, Providence city gas	42.7	10	1.7	27.3*	0.5	15.1
Burned 3:1 ratio	20.0	10	4.5	3.5	...	Balance
Matthews and Biemiller[4]						
Baltimore city gas, 2.8:1 ratio	13.9	5.8	9.5	...	...	Balance
Partly burned Detroit city gas**	28.0	14.0	3.0	7.0	...	Balance
City gas, cracked with very little air	60.0	15.0	4.0	8.0	...	Balance
Battelle, Columbus natural gas	...	...	1.2	83.0***	0.6	15.2
Burned 4.3:1 ratio (not commercial)	26.0	14.0	3.0	6.0	...	Balance
Heyn, Toledo natural gas, 6:1 ratio	9.6	8.7	5.8	1.9	...	Balance
Krogh, propane, 12:1 ratio, 2000° F.	8.0	10.0	8.0	1.0	...	Balance
Commercial propane, 12:1, 1700° F.	13.0	11.0	7.0	1.0	...	Balance
Coke oven gas	56.9	8.7	3.0	25.6	...	Balance
Above burned, 2.5:1 ratio	6.0	6.0	6.0	1.5	...	Balance
Burned, commercial	9.1	12.9	5.6	1.3	0.2	Balance
Other commercial gases:						
Cracked ammonia	75.0	...	...	...	...	Balance
Gas from propane, chemically treated****	5 to 10	...	...	trace	...	Balance
Dry gas producer, from charcoal	1.0	31.0	2.0	trace	...	Balance

* Also 2.7% illuminants.
** For skin carburizing of gears—hydrocarbon may be added if a thicker case is desired.
*** 68.9% CH_4, 9.9% C_2H_6, and 4.2% C_3H_8.
**** Similar gas may be produced by partly burning cracked ammonia and removing moisture.

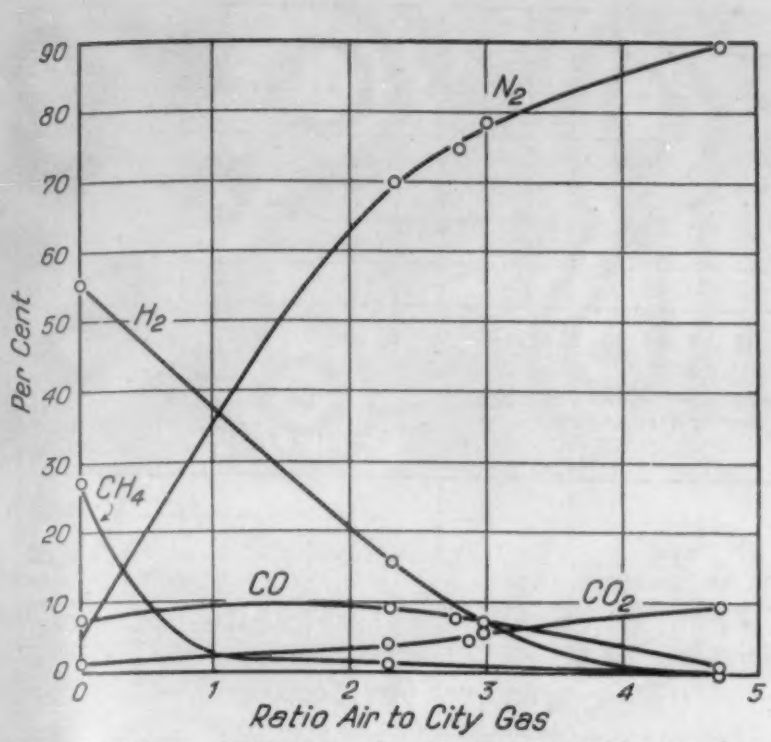


Fig. 1—Effect of Varying the Air Ratio on the Products of Partial Combustion of City Gas. (Marshall)

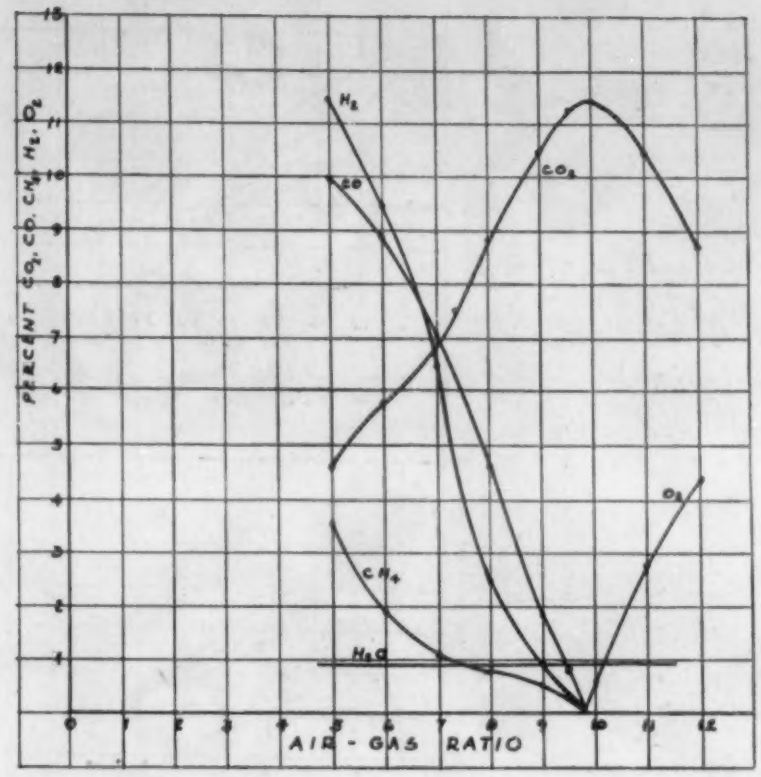


Fig. 2—Effect of Varying the Air Ratio on the Products of Partial Combustion of Natural Gas. (Heyn)

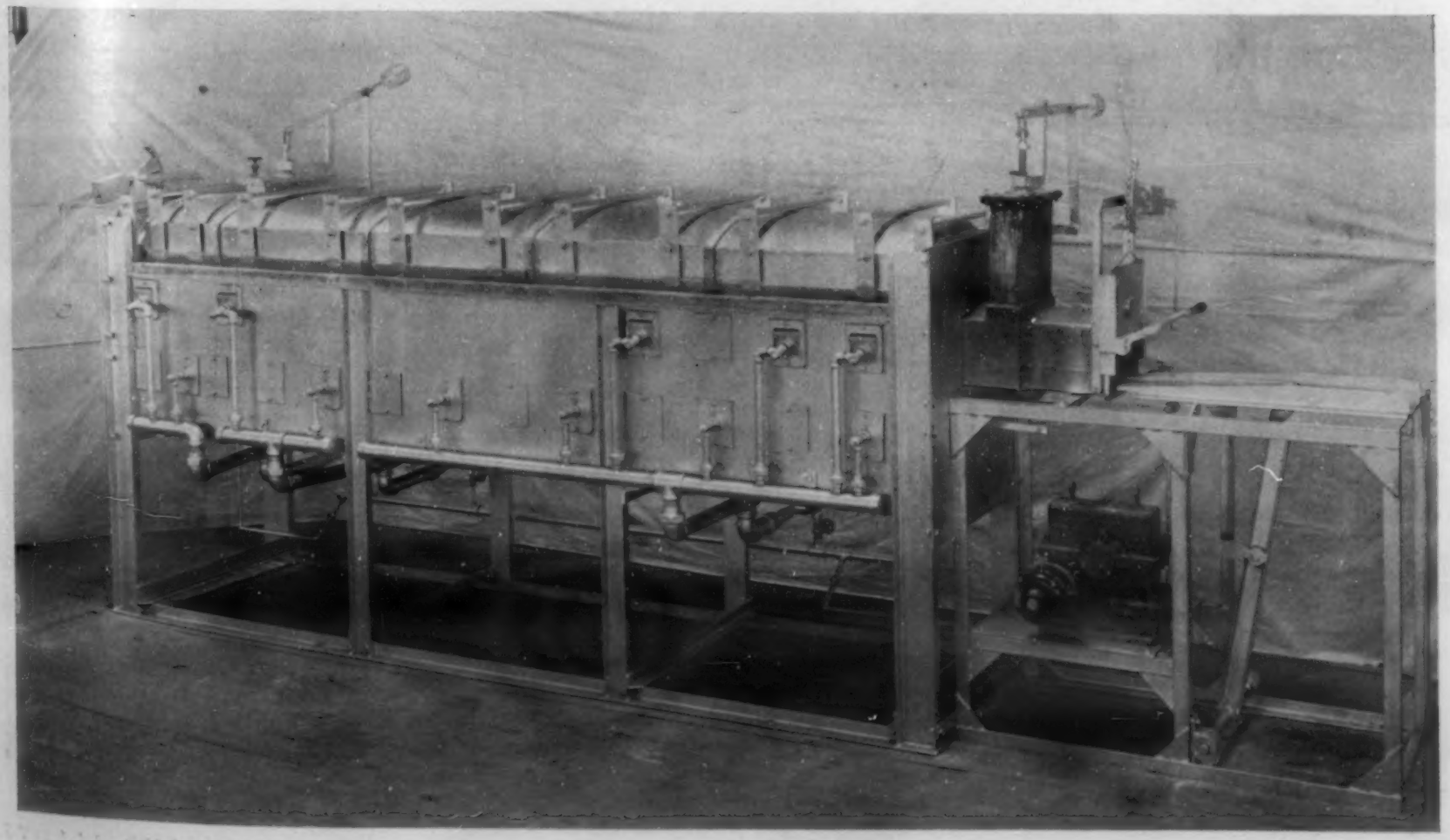
gas similarly made and used for burning of porcelain ware. For copper annealing, Holler[8] considers the dry charcoal producer to give a very desirable gas, low in H_2 and CO, if burned at about 550 deg. C. (where gas left the producer).

Miscellaneous Gases

Various atmospheres may be produced by cracking suitable hydrocarbons. Methanol, for example, on decomposing at 1600 to 1800 deg. F. breaks down into about 58 per cent H_2, 31 per cent CO, 6.5 per cent CO_2, 3 per cent CH_4, and some water vapor. By cracking such hydrocarbons as methane, propane, butane, and various oils and permitting the soot to separate in the cracking unit, an effluent gas of about 10 to 20 per cent CH_4, balance H_2, is obtainable. By a roundabout method of partly burning a fuel gas like propane, adding steam and passing the resultant gas over a catalyst to oxidize CO to CO_2 and release H_2, then removing the CO_2 by absorption (Kinzel quoted by Gillett)[9], a gas may be produced that is low in hydrogen and very high in nitrogen, with possibly a little CH_4 present.

Liquid NH_3 may be cracked by heating to form a gas of 75 per cent H_2, 25 per cent N_2 composition. This, in turn,

A Full Muffle Heating Machine with a Charging Vestibule and Inner Door, and a Discharge Vestibule under Heat for Quenching from Temperature. (Courtesy: American Gas Furnace Co., Elizabeth, N. J.)



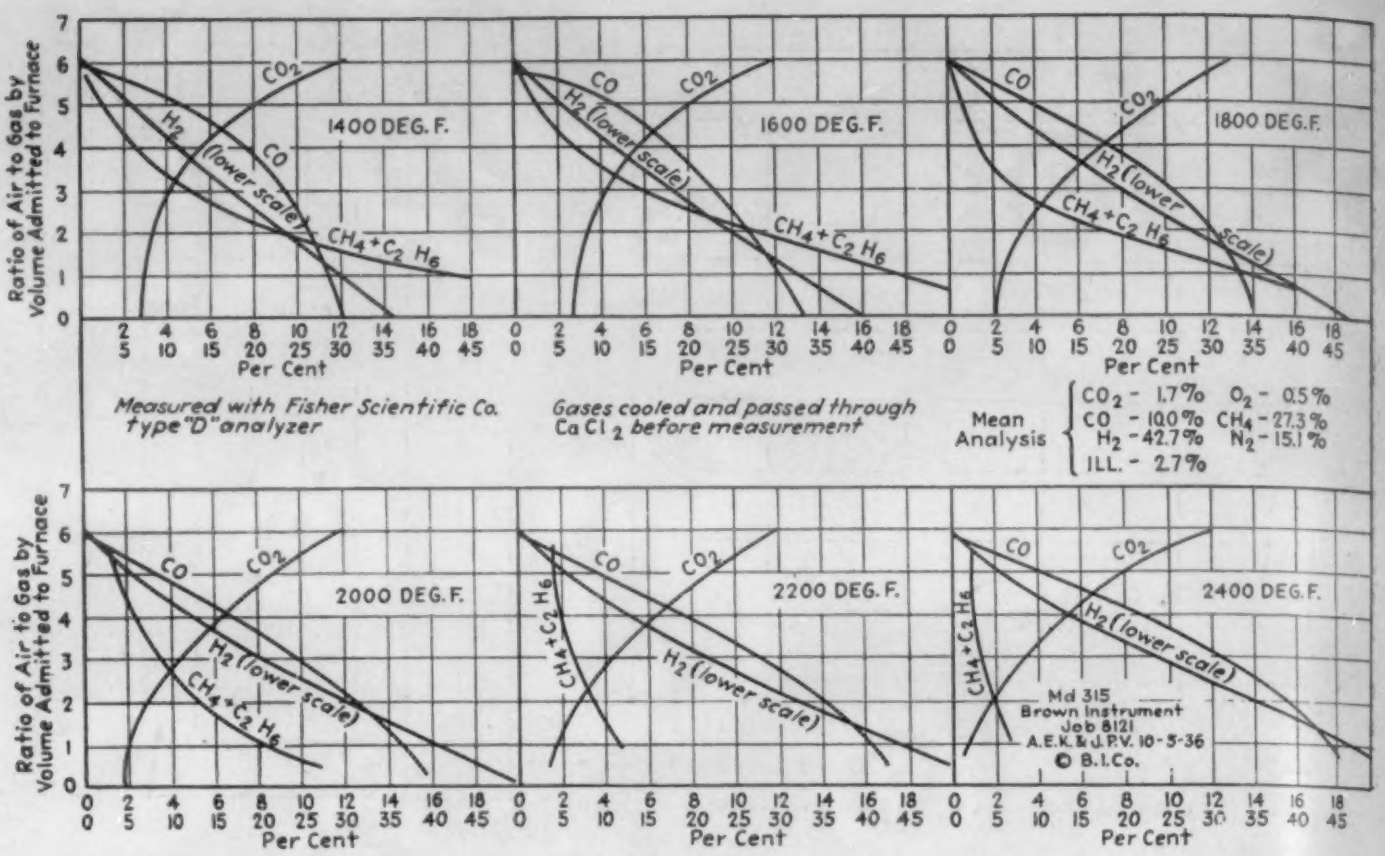


Fig. 3A — Change in Composition of Products of Combustion of City Gas with Varying Air Ratios and Temperatures of Combustion. (Krogh)

may be partly burned with air and water vapor removed to give a low hydrogen gas, as 5 to 10 per cent H_2 with balance N_2. Such cracked, or cracked and partly burned, NH_3 is used commercially in the annealing of silicon steel sheet.

Compressed gases (in cylinders) or relatively pure gases generated on the spot, as H_2, N_2, CO, and even He, are often used experimentally, with suitable purification to remove traces of O_2. Occasionally such relatively expensive gases are used in very small scale commercial annealing processes.

GAS REACTIONS

The behavior of the pure gases and of the $CO:CO_2$, $H_2:CH_4$, and $H_2:H_2O$ mixtures toward steel is fairly well known. Gillett[9] has summarized the reactions in his correlated abstract on controlled atmospheres.

Pure CO is a weak carburizer. Without an energizer in pack carburizing, carbon surrounding the work reacts with the air in the box to form a $CO:CO_2$ mixture like that mentioned above from a dry gas producer. Due to the lack of gas flow, however, the $CO:CO_2$ ratio more nearly approaches the theoretical for the carburizing temperature. This is calculated to be a gas of about 33 per cent CO, 0.5 per cent CO_2, balance N_2. Such a gas will carburize low carbon steel but it is known to be difficult to obtain hypereutectoid cases with non-energized charcoal. In other words, such a gas is only weakly carburizing to approximately eutectoid and higher carbon steels. Becker[10] gives data on $CO:CO_2$ equilibrium with various steels, shown in Table II.

When the amount of CO present is greater and that of CO_2 less in contact with carbon than with a given steel, the steel will be carburized by the gas. When the opposite

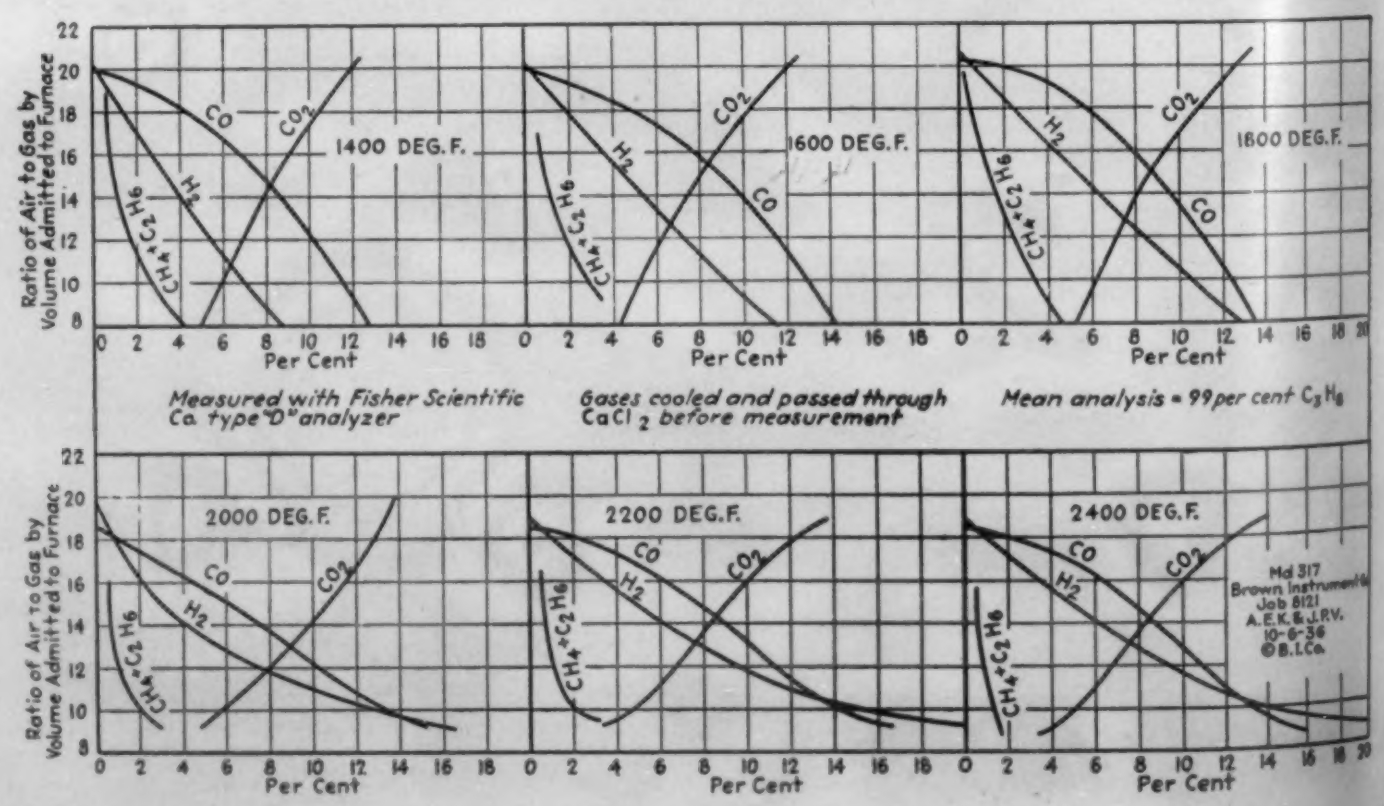


Fig. 3B — Change in Composition of Products of Combustion of Propane with Varying Air Ratios and Temperatures of Combustion. (Krogh)

occurs, or the CO_2 in equilibrium with carbon is greater than it is with a certain steel, decarburization occurs. Thus, as seen in Table II, all the steels in a carburizing box with

Table II.—Percent CO_2 at Equilibrium in Contact With— (Balance Is CO)

Temperature						
Deg. C.	Deg. F.	Graphite	1.2% C Steel	0.8% C Steel	0.4% C Steel	0.1% C Steel
650	1200	62.6	55.7	55.7	55.7	55.7
750	1380	26.3	21.8	25.1	28.5	28.5
850	1560	5.85	5.7	7.1	12.5	26.7
950	1740	1.5	2.0	2.9	4.8	14.2

carbon tend to be decarburized at 1200 deg. F., and even at high carburizing temperatures the urge to carburize high carbon steels is very slight.

Decarburization also occurs in the absence of carbon when the CO_2 present is above the equilibrium ratio given in the Table for a particular steel at a given temperature. As an example, a gas of 28 per cent CO, 2 per cent CO_2 balance N_2 (ratio of 6.7 CO_2:93.3 CO) at 1740 deg. F. will decarburize steel containing around 0.4 per cent C or more but will carburize 0.10 per cent C steel. Moisture disturbs the ratio and accelerates action, particularly decarburization.

In the case of the H_2:CH_4 ratio of gases, data are cited by Austin[11] to show that at 1830 deg. F. a gas of 99 per cent H_2, 1 per cent CH_4 is in equilibrium (i.e., neither carburizing nor decarburizing) with steel containing about 1 per cent C. With only 0.1 per cent CH_4 present, equilibrium is established with a 0.15 per cent C steel. Moisture also disturbs this equilibrium.

Dry H_2 is slightly decarburizing to high carbon steel and has practically no action on low carbon steel, but with moisture present decarburization is vastly increased, as shown by Austin and others. When the ratio of H_2O to H_2 is sufficiently high, as 60 H_2O:4O H_2 at 1700 deg. F., steel is oxidized, forming scale. This scaling effect becomes more pronounced as the temperature drops; at 1200 deg. F., 37 H_2O: 63 H_2 causes scaling. Since it is the ratio rather than the percentage content that counts, a mixture of 6 per cent H_2, 94 per cent N_2 need carry only about 2 per cent H_2O (corresponding to a dew point of 65 deg. F.) to scale steel at 1200 deg. F. and still less at lower temperatures. In bright annealing in hydrogen where the steel is cooled to room temperature in the gas, as a consequence great care must be taken to avoid the presence of moisture or tarnish or even scale will result.

The composition of the gas formed in commercial water gas producers is such as to indicate that the reaction between water vapor and carbon does not have time to reach equilibrium. The same may be true of many partly burned fuel gas producers. When gases from such producers are led into a heat-treating furnace, however, conditions are favorable for continued reaction. It is this change in gas composition

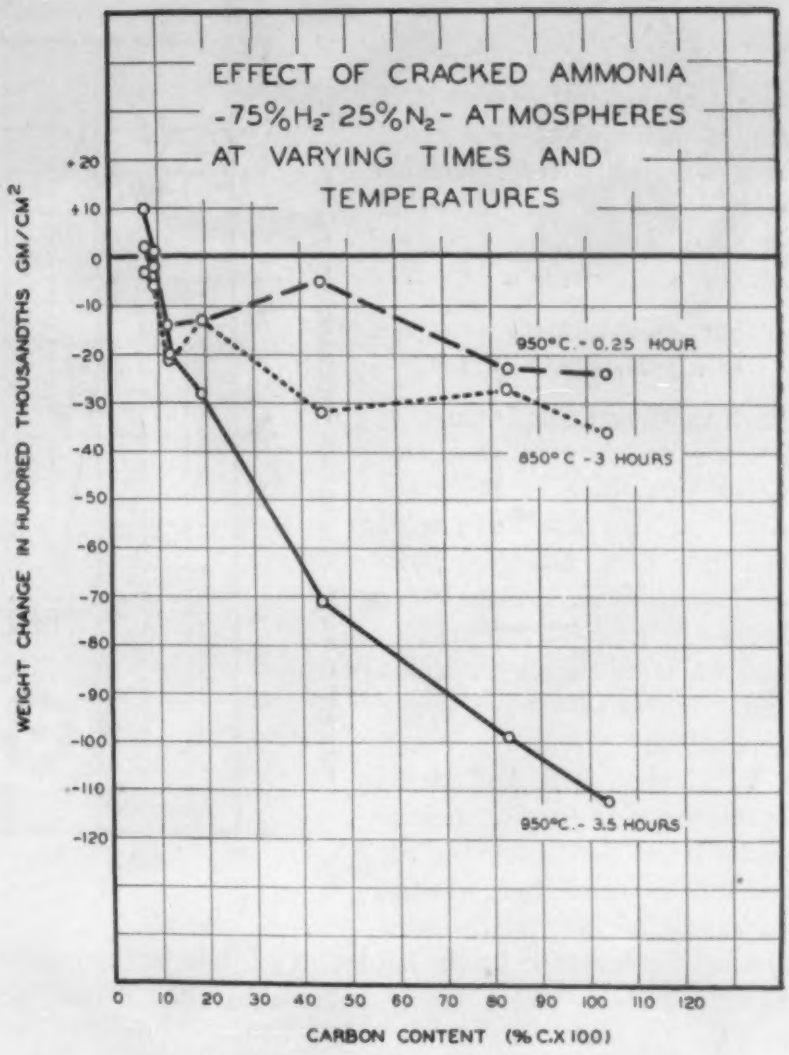
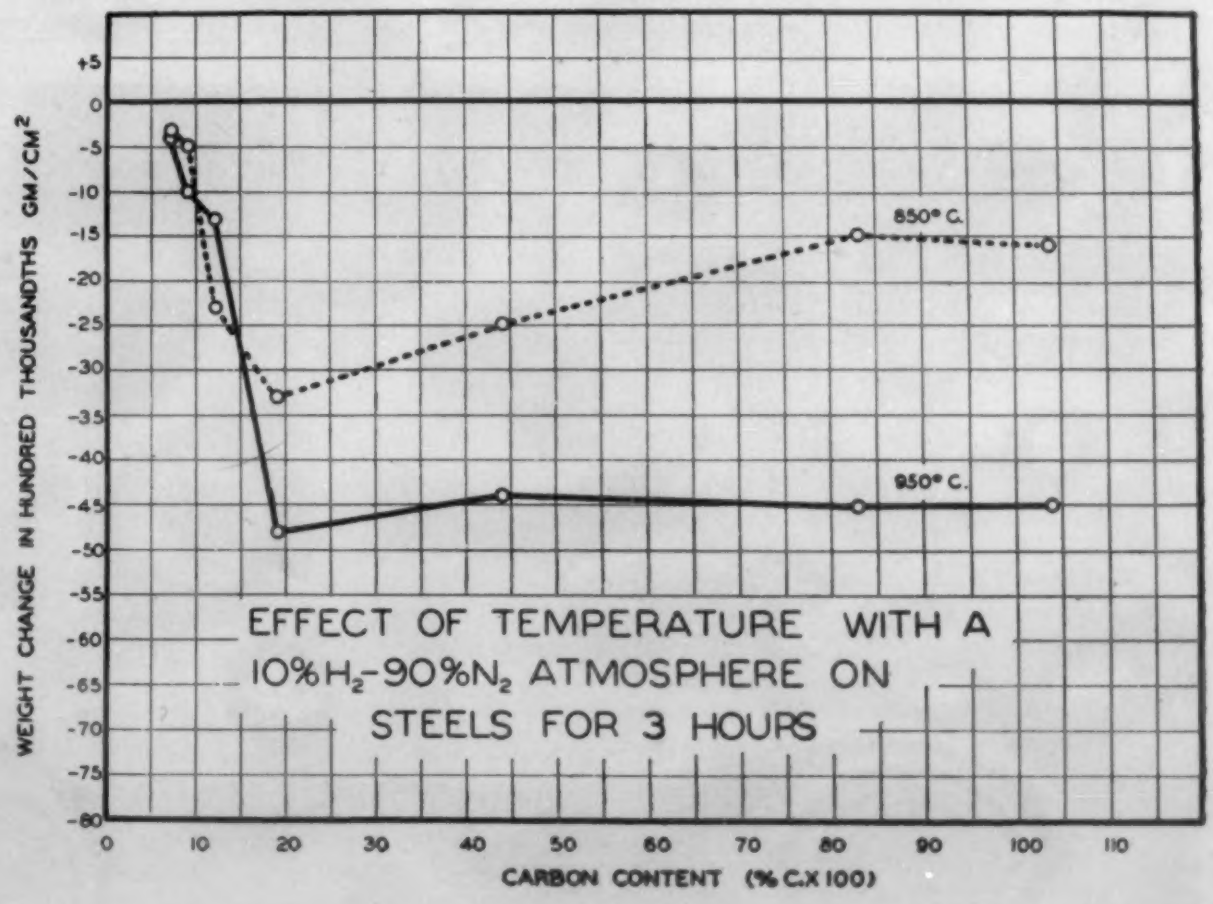


Fig. 4

in the furnace that is particularly objectionable. A preheater to give the gas a chance to react more completely before touching the work is one means of avoiding unnecessary trouble with such gas.

Marshall[2] studied, in great detail, the use of partly burned fuel gas mixtures for bright annealing of low carbon steel at 1200 deg. F. He points out that even though

Fig. 5



no carburization or decarburization of the low carbon steel results in these complex gases, and the steel surface remains clean, it may yet become dulled (matted) by acting as a catalyst for the reactions:

$$2CO = CO_2 + C$$
$$CO_2 + H_2 = CO + H_2O$$

In bright hardening there is not the necessity for a mirror finish that there is in bright annealing, but this reaction of H_2 with CO_2, catalyzed by a steel surface, is of importance because it leads to the production of H_2O which, as stated above, makes H_2 act as a strong decarburizer.

It is recognized, and stated by Heyn[2], that the commercial partly burnt fuel gases used for controlled atmosphere bright annealing of low carbon steel are not applicable to bright hardening of 0.40 per cent and higher carbon steel when decarburization is to be avoided.

A wide range of gas compositions is applied to bright annealing of low carbon steels. Some of these gas compositions seem to be injurious to resistor elements and heat-resistant alloys. It would be desirable, therefore, to find gases for controlled atmospheres that will allow the heating for quenching or normalizing of medium and high carbon steels without either sealing or decarburization, and that are not injurious to resistors, conveyors, and the like.

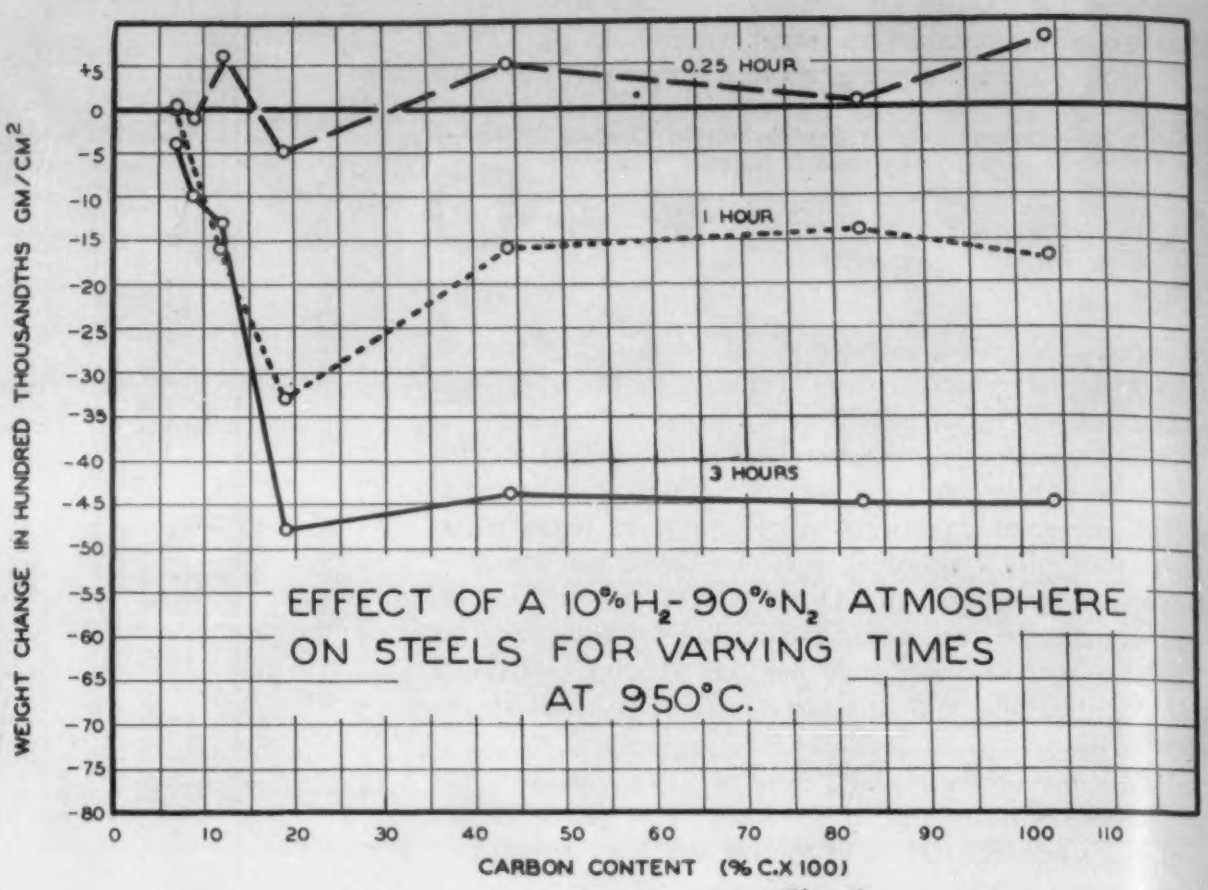
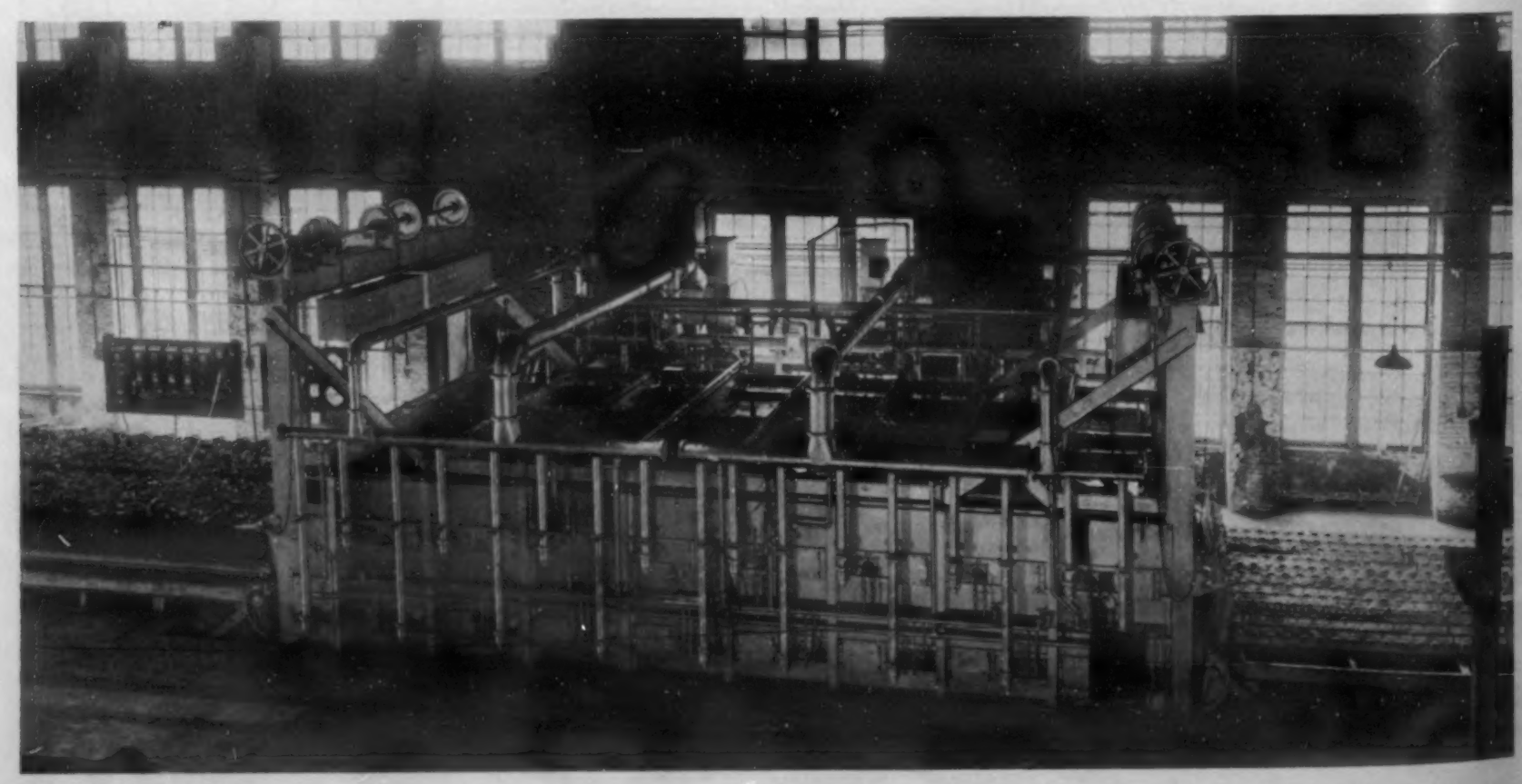


Fig. 6

EXPERIMENTAL WORK

In view of the difficulties in applying controlled atmospheres to bright hardening, a promising field of research appeared to be a study of the behavior of typical commercial protective atmospheres on higher carbon steels and at higher temperatures than those studied by Marshall.[1] Exploration of the possibilities of adjusting the gas compositions to avoid the fatal decarburization so often encountered in this field, was also a consideration. A preliminary study of this problem was undertaken by Battelle Memorial Institute; the present phases are sponsored by Utilities Co-

A Batch Type Malleabilizing Furnace Heated by Means of Gas-Fired Radiant Tube Heating Elements. The protective atmosphere is prepared in a Surface Combustion DX unit. (Courtesy: Surface Combustion Corp., Toledo, Ohio.)



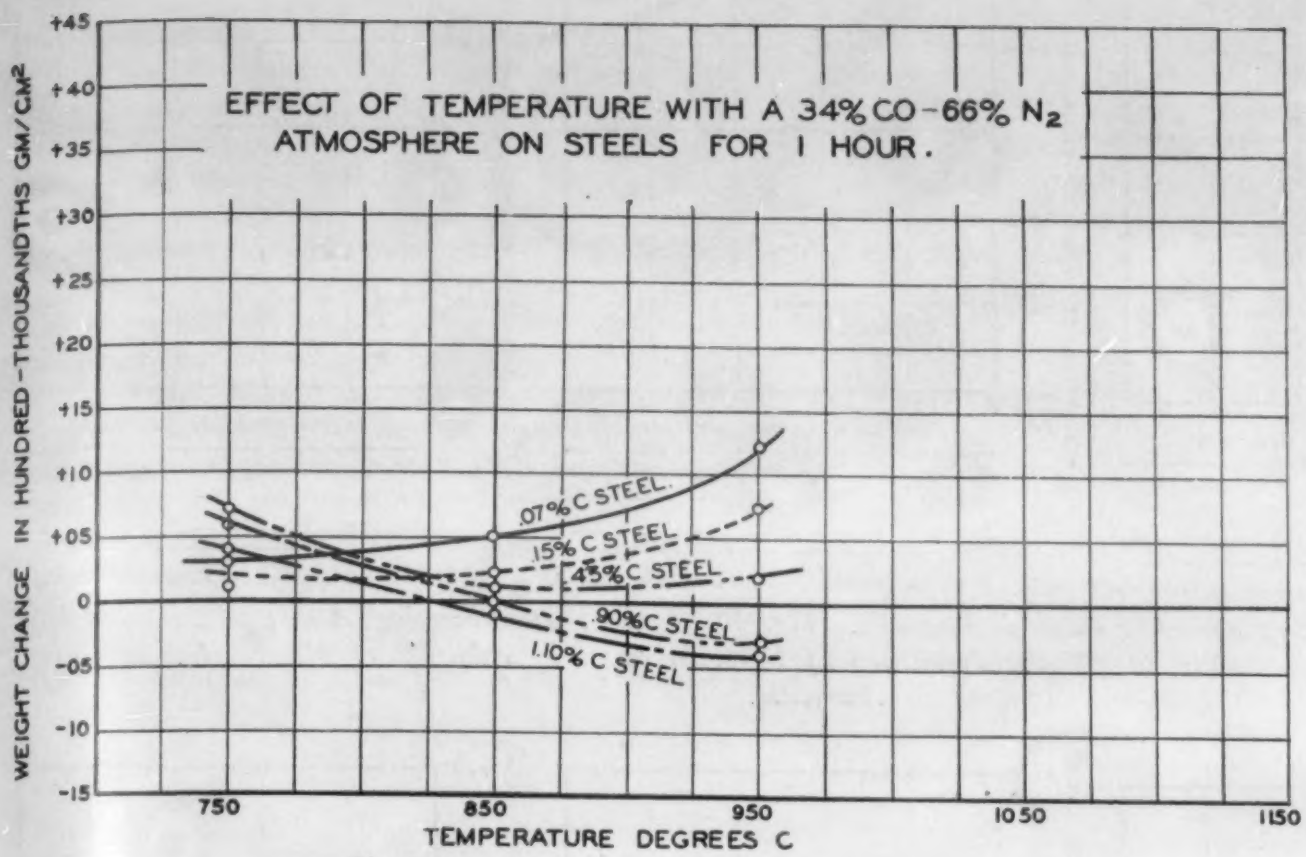


Fig. 7

ordinated Research, Inc. This may be considered a progress report on the joint project.

Acknowledgements

The various phases have been carried out under the general direction of H. W. Gillett, the earlier work largely by N. K. Koebel[12] and R. E. Parkinson. Mr. Parkinson's assistance throughout the later phases is also gratefully acknowledged.

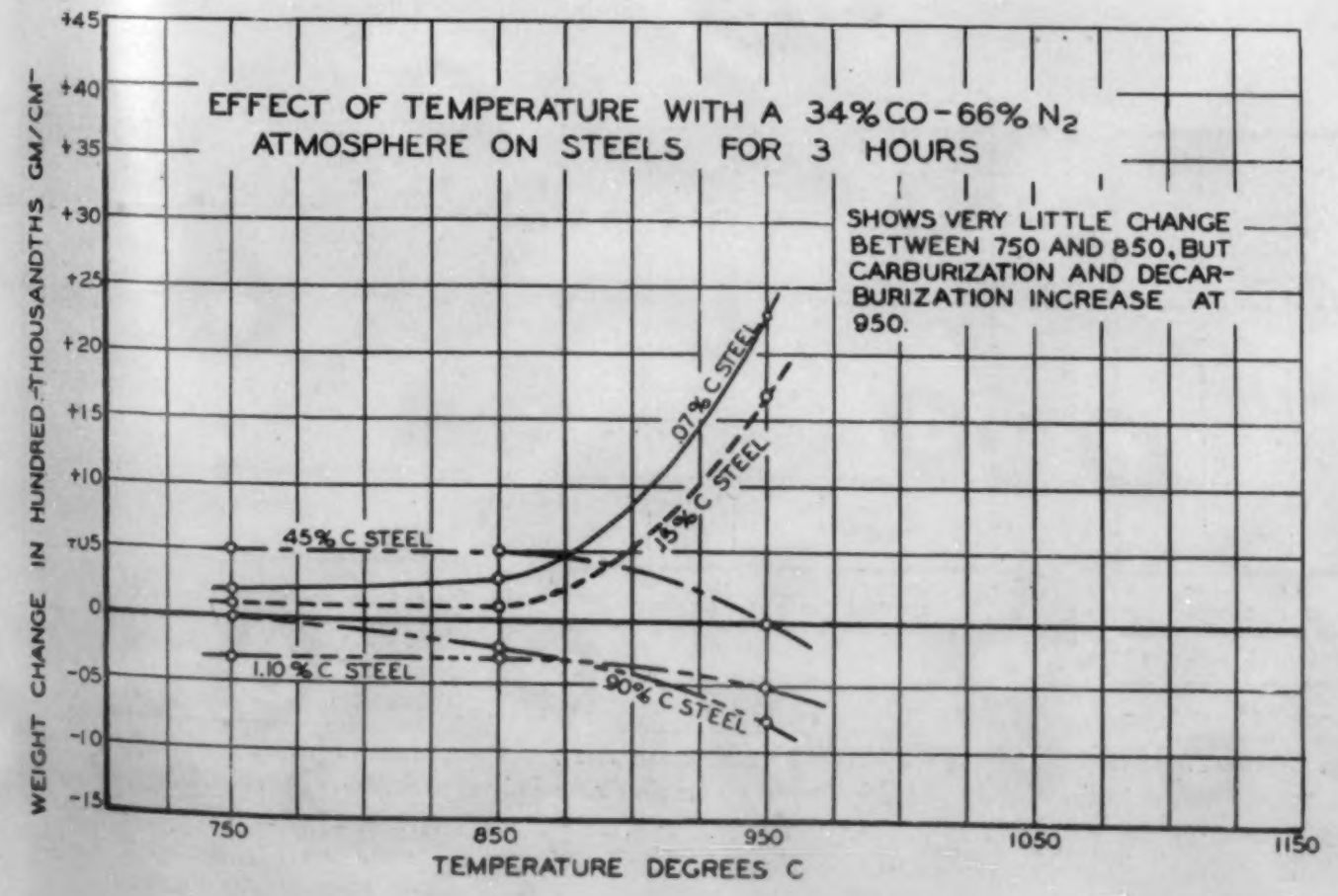
Materials and Procedure

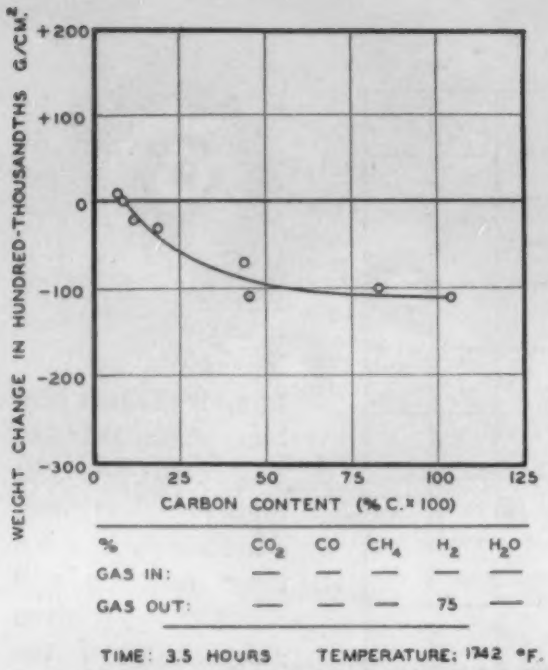
Any such study must start with plain carbon steels. It is recognized that some alloy steels will behave quite differently, and that high speed steel, in particular, is a problem by itself. As a beginning, it was decided to study carbon steels ranging from 0.07 to 1.04 per cent C. A difficulty arose in that, in a given gas mixture, the lower carbon steels may be carburized and the higher carbon ones decarburized, and these reactions will slightly alter the composition of the gas within the furnace. However, the ultimate goal is a gas in which none of the steels are appreciably affected, so if this is really reached, the presence of specimens of varying carbon content is allowable. When it is not reached, the presence of varying specimens modify, but should not obscure the effect of the gas. At any rate, the work would be so prolonged by making individual tests upon steels of several carbon contents that the testing of several steels in the furnace chamber at one time was adopted. The low carbon steels, normally less decarburized than the high carbons, were put at the end of the furnace at which the gas entered, except in certain cases as noted.

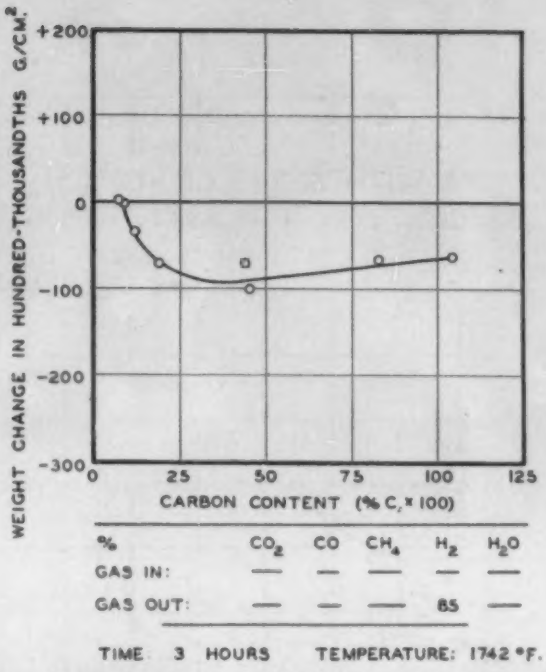
The steel specimens used in this work were heated in a 1¾ in. I.D. McDanel dense porcelain tube, externally heated by an electric resistor tube furnace having a winding of 1400 watts maximum capacity. Temperature was controlled by means of a thermocouple and automatic controller.

Gases used were largely synthetic, prepared from pure components and mixed in the ratio desired. Cylinder H_2 and N_2 were purified by passing over copper chips held at 750 deg. C., then dried by $CaCl_2$ and P_2O_5. Sometimes H_2 was made from Zn and HCl, then passed over soda lime, $CaCl_2$ and P_2O_5. Cylinder CO_2 was merely dried over $CaCl_2$ and P_2O_5 before using. Natural

Fig. 8







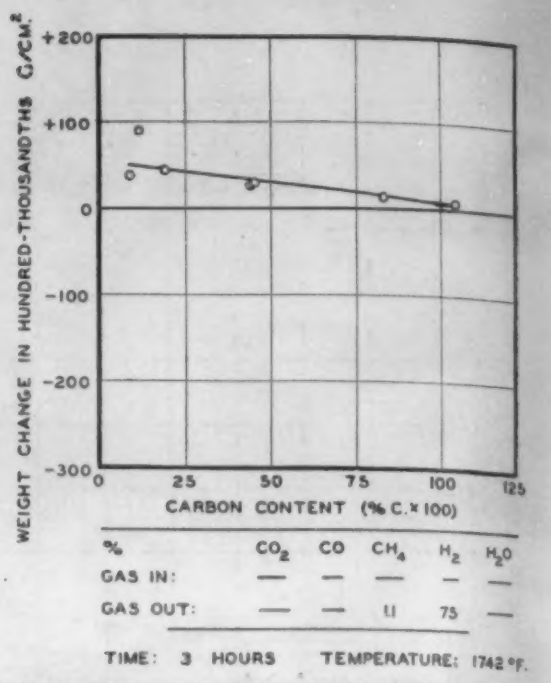
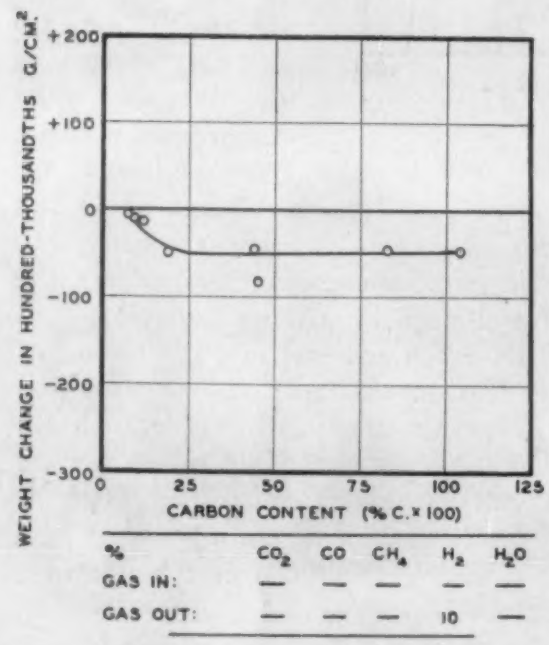
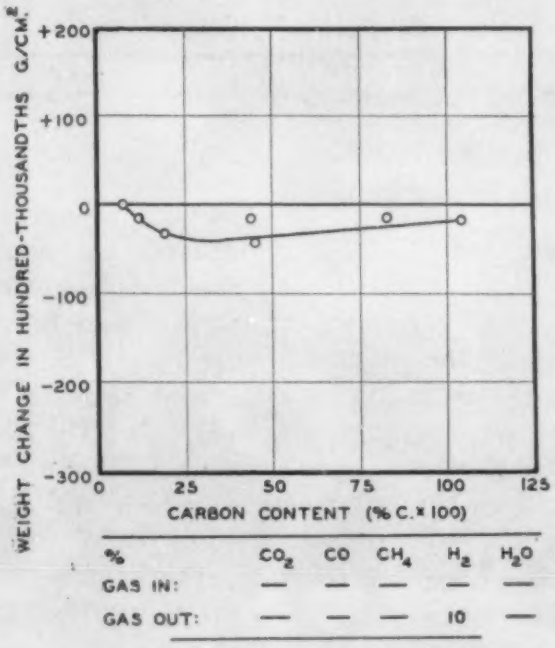


Fig. 9 (Left) Decarburizing Action of Cracked Ammonia. Fig. 10 (Center) Decarburizing Action of Synthetic High Hydrogen-Nitrogen Mixture. Fig. 11 (Right) Prevention of Decarburization by Addition of Natural Gas to Cracked Ammonia.





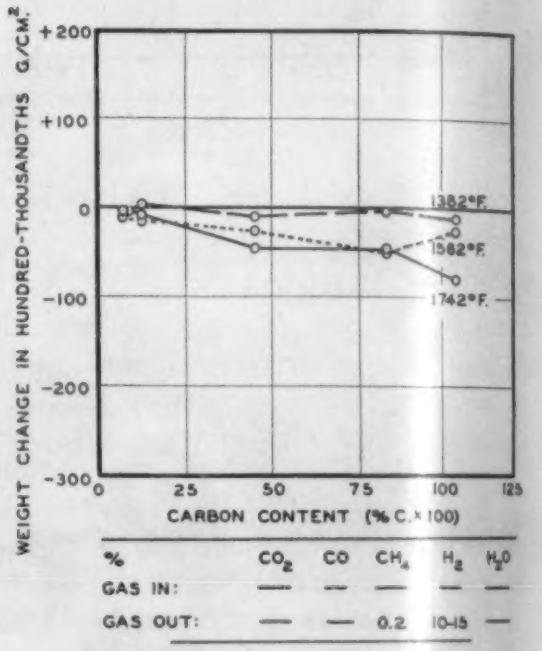
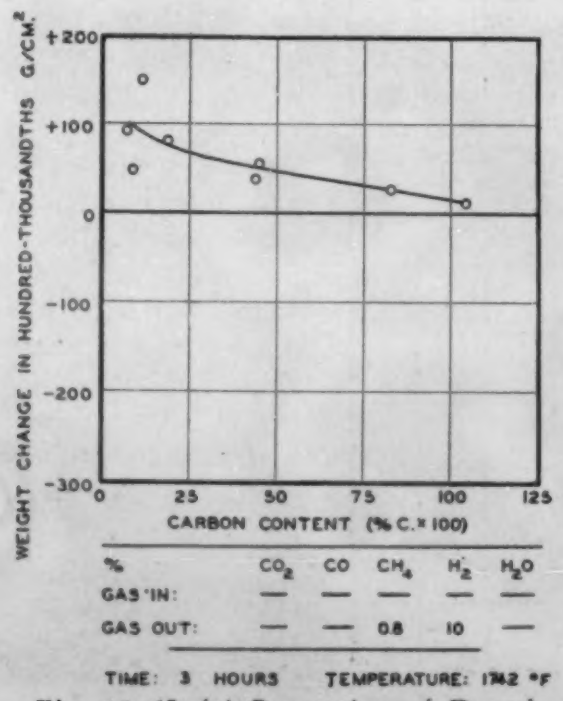
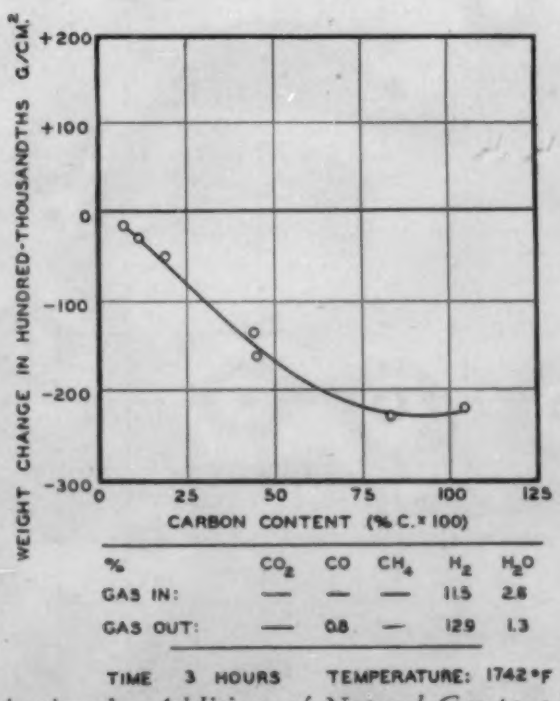


Fig. 12 (Left) Effect on Decarburization of a Low Hydrogen Content, in a Hydrogen-Nitrogen Atmosphere. Compare with Fig. 9. Fig. 13 (Center) Effect on Decarburization of a Shorter Period of Treatment, in a Low Hydrogen-Nitrogen Atmosphere. Fig. 14 (Right) Effect of Varying Temperatures on Decarburization, in a Low Hydrogen-Nitrogen Atmosphere.





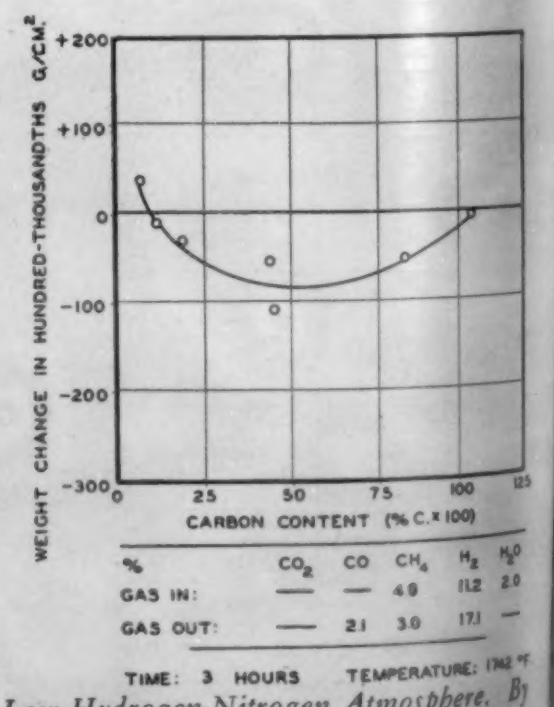


Fig. 15 (Left) Prevention of Decarburization by Addition of Natural Gas to a Low Hydrogen-Nitrogen Atmosphere. By adjustment of CH_4 this could be made neutral to any carbon steel. Fig. 16 (Center) Action of Moisture in Accelerating Decarburization, in a Low Hydrogen-Nitrogen Atmosphere. Enough C was removed from the steels to show up as CO in the exit gas. Samples stained. Fig. 17 (Right) Effect of Adding Natural Gas to a moist Low Hydrogen-Nitrogen Atmosphere, Low Carbon Steels at Gas Inlet. Specimens stained.

gas was used as the source for methane. It was purified by passing over phosphorus and the regular drying agents. Carbon monoxide was made from formic and sulphuric acids, passed through alkaline pyrogallol and over phosphorus, dried with $CaCl_2$ and P_2O_5 and finally passed over electrode carbon at 1100 deg. C. The CO was stored in a mercury sealed gasometer before final drying and heating with carbon; the other gases were made or supplied from tanks as needed. When water vapor was desired in the gas mixture, the incoming gas was passed through a water bottle held at a definite temperature corresponding to the amount of vapor desired. Gases for some tests were made from a dry gas producer or from other devices; in some tests cracked NH_3 was used. The flow of gases was controlled by accurately calibrated flow meters and the desired mixture introduced into the furnace at a constant rate of 150 to 160 cc. per min.

Table III.—Analyses of Steels Used in Experimental Work

		Composition, Per Cent								
Class	Shape	C	Mn	Si	S	P	Cr	Cu	Ni	Sn
AA	Flat strip	0.07								
A	Flat strip	0.09	0.37	0.02	0.029	0.017	0.02	0.057	0.039	0.007
B	Cyl.	0.12	0.76	0.02	0.17	0.082	0.02	0.059	0.009	0.004
G	Cyl.	0.19	0.91	0.15	0.154	0.018	...	.....	.....	.....
C	Cyl.	0.45	0.66	0.05	0.028	0.018	0.02	0.049	0.005	0.003
H	Cyl.	0.44	0.73	0.18	0.040	0.016	...	.....	.....	.....
D-1	Block	0.83	0.47	0.21	0.022	0.016	0.05	0 186	0.056	0.021
D-2	Cyl.	0.87	0.49	0.24	0.032	0.040		after run 134		
E	Cyl.	1.04	0.34	0.15	0.012	0.016	0.03	0.150	0.049	0.025
E-2	Cyl.	1.02	0.29	0.18	0.027	0.016	0.04	0.083	0.036	0.010
								after run 132		

It was noted that the "C" 0.45 C steel was very readily decarburized. Another 0.45 steel, "H", was then procured and both steels used in later tests. The "H" steel was usually less readily decarburized.

These specimens were cleaned with emery paper, washed in alcohol, dried and weighed before being inserted into the cold furnace tube. After flushing the tube with the gas to be used until no free O_2 could be detected in the exit gas, the furnace was heated to the desired temperature, held there for a desired time interval, and cooled with the same flow of gas maintained. Usually the specimens were cooled in position in the furnace, but in some of the later runs they were wired together and pulled into the unheated exit end of the tube for more rapid cooling. With some of the complex gases studied, enough moisture was formed by reaction to bring in the possibility of staining on slow cooling, which would not occur on quenching or normalizing.

General Effect of Time and Temperature

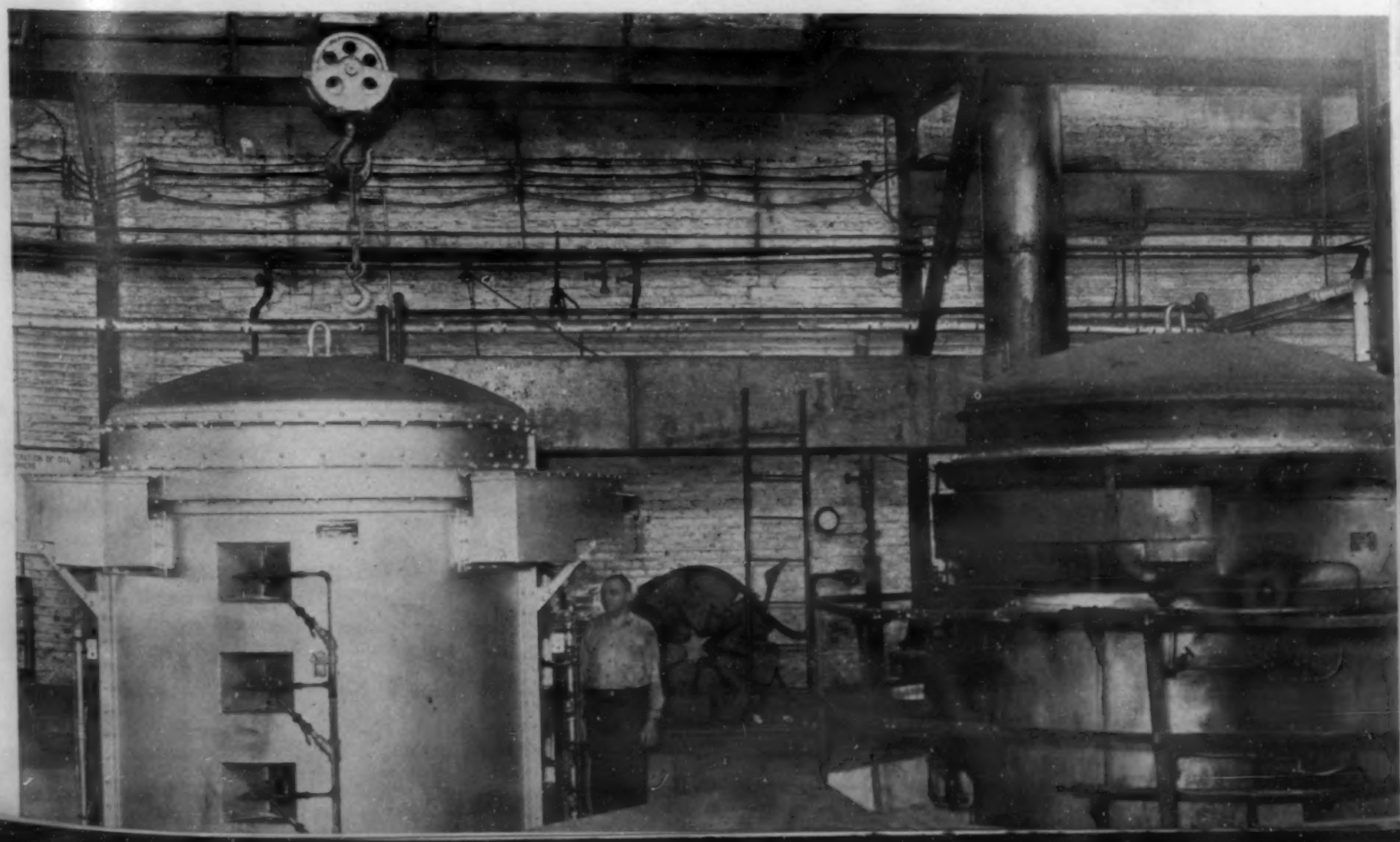
The choice of a practical temperature was difficult since proper quenching or normalizing temperatures for the lower carbon steels would be above the normal temperature for those operations on the higher carbon steels. Three temperatures were consequently used, 750, 850, and 950 deg. C. (1380, 1560, and 1740 deg. F.). Time intervals were varied from ¼ to 3 hrs.

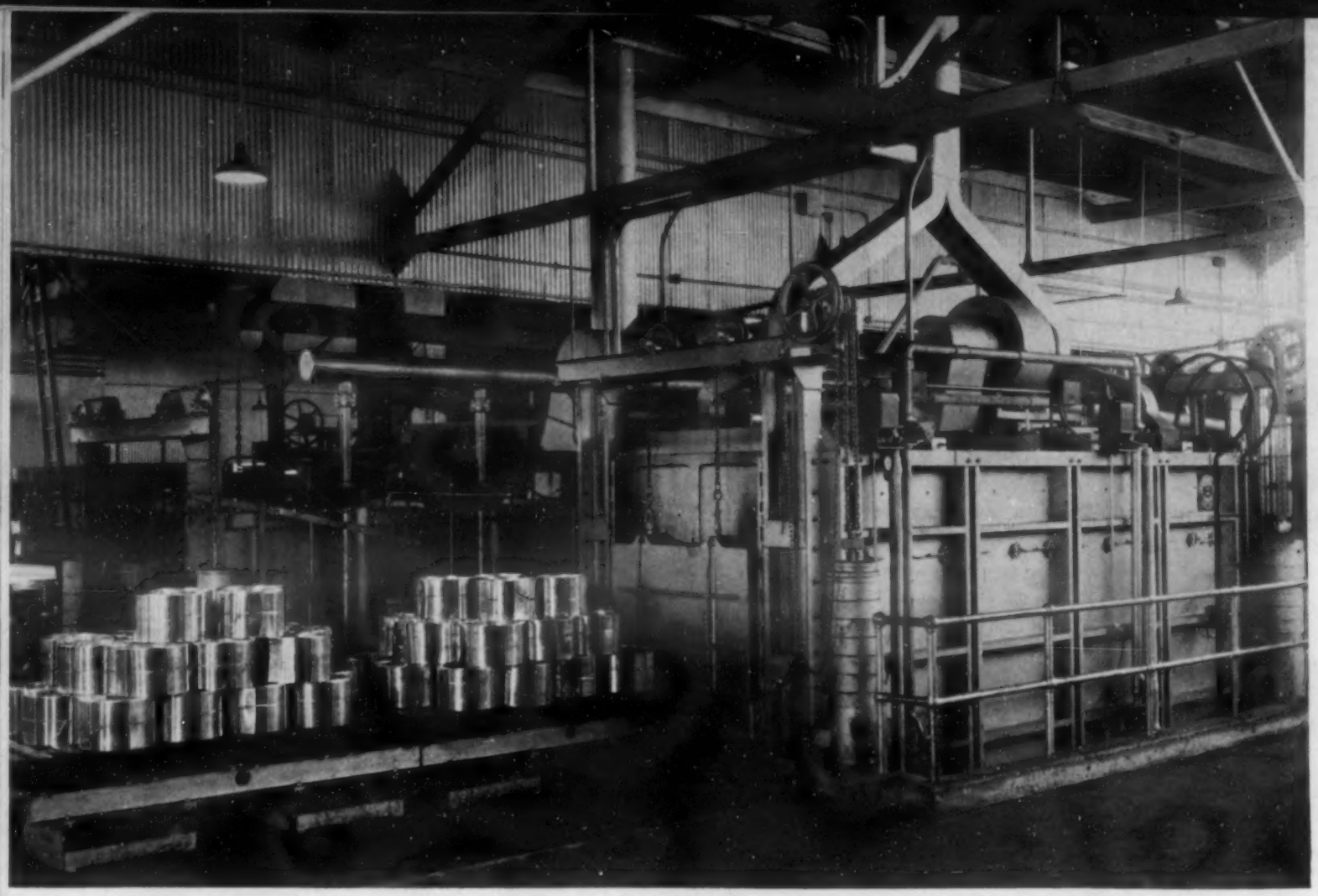
Figs. 4 to 8 show the effect of varying time and temperature for 75 per cent and 10 per cent H_2 and for 34 per cent CO. In these simple gases, at least, it appears that a carburizing or decarburizing tendency of the gas is exaggerated by using the higher temperatures and longer time, hence the bulk of the investigation was made at the extreme of 3 hrs., at 1740 deg. F. in order to secure the exaggeration.

The fact that some of the atmospheres used would not show deleterious effects in the shorter time intervals and at the lower temperatures required in commercial heat treatment, should be remembered in considering the results of these tests.

As usual in work of this kind, connections would spring a leak from time to time and traces of air would be admitted. Unless the gas mixture itself was obviously reacting to stain the specimen, all runs so vitiated by leaks as shown by stained specimens, were discarded and the tests repeated.

Battery of Continental Pot Type Bright Annealers. (Courtesy: Continental Industrial Engineers, Inc., Chicago.)





Recirculating Muffle Type Coil Annealing Furnace. (Courtesy: W. S. Rockwell Co., New York.)

Such accidents served to make very impressive the fact that many of the gases are extremely sensitive to contamination by traces of free oxygen from the air.

Method of Reporting Results

As a quantitative measurement, the degree of carburization and decarburization of the samples treated is reported in terms of gains or losses in weight per unit of surface area. These are plotted above and below a zero line; points above the line indicate a gain in weight due to carburization, points below show decarburization. This holds true since there was no scaling in any of the tests reported unless so stated. Metallographic examinations were made from time to time which verified this assumption. The weight changes were found to be more sensitive than the microscope. In general, a weight gain or loss of 0.00010 gms. per sq.cm. was necessary for carburization or decarburization to be evident by microscopic examination, even on the low carbon steels. For all practical purposes, consequently, weight changes of $\pm$ 0.00010 gms. per sq.cm. can be considered as an absence of any appreciable effect of the gas on the steel.

Duplicate runs were made at various times after making alterations and repairs to the equipment, and check tests were made by three observers. As the curves will show, these usually gave quite consistent results. Indeed, the points for the two 0.45 per cent C steels showed as much and often more variations in individual runs than did the position of a given curve in duplicate tests.

Hydrogen-Nitrogen Mixture

The decarburizing action of cracked ammonia is shown in Fig. 9. Practically the same effects are shown by Fig. 10, in which a synthetic mixture of H_2 and N_2 is used. That a small amount of CH_4 makes the cracked NH_3 carburizing, is shown in Fig. 11. The difference in degree of carburization of the 0.07 and 0.12 per cent C steels is probably due to their differences in shape and position in the furnace. The 0.12 per cent C specimen, being located at the point of entrance of the gas, was in a position for maximum carburization, whereas the 0.07 per cent C strip extended along the tube beyond this zone of gas composition changes.

Fig. 12 shows reduced decarburization upon reducing the concentration of H_2 to 10 per cent, while Fig. 13 shows reduced decarburization upon dropping the exposure time to 1 hr., and Fig. 14 demonstrates the reduction in decarburization upon going to lower temperatures. The presence of 0.8 per cent CH_4 in the exit gas made this 10 per cent H_2 atmosphere carburizing to all the plain carbon steels, as shown in Fig. 15.

The question of the effect of moisture, or of infiltered air that would combine with H_2 to form H_2O, was studied. The effect is shown in Fig. 16. The H_2O reacted with the steel reducing the amount of H_2O in the exit gas by half and producing 1.4 per cent more H_2 and 0.8 per cent CO. As expected, the decarburization was greatly accentuated. The next question is, can this decarburization be neutralized by addition of CH_4?

As Fig. 17 shows, 5 per cent CH_4 produced carburization on the lowest carbon steel and practically eliminated decarburization on the highest, but did not greatly help the 0.45 per cent steels. With 8 per cent CH_4, as in Fig. 18, the whole curve is shifted, accentuating both carburization and decarburization. The specimens were stained, and not only the H_2O, but the CH_4 entered into reaction. The difference in the shape of these two curves is undoubtedly due to the fact that the inlet gas hit the low carbon steels first in the former run (Fig. 17) while it hit the high carbon steels first in the latter, thus illustrating the importance of the gas reaction within the atmosphere. The compositions of the incoming and outgoing gases are shown on the figures.

While dry H_2 or H_2:N_2 mixtures can be prevented from decarburizing and forced to carburize all the steels by addition of CH_4, moist H_2, to which enough CH_4 has been added to produce carburization of low carbon steels, still is decarburizing to medium and high carbon steels.

(To be concluded)

AN IMPROVED METHOD OF STUDYING

Inclusions in Alloy Steels

by W. A. Hare and Gilbert Soler

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A method of study of inclusions present in certain alloy steels is described in which the analysis and actual mineralogical phases present are determined by chemical and petrographic means, supplemented by X-ray studies if necessary. The value of the information in regard to steel manufacture is briefly noted. Results of study of several types of alloy steel are given with photomicrographs of two typical inclusions.

INCLUSIONS IN STEEL may be defined as particles of a separate phase of non-metallic nature adventitiously present in the steel. In general, they may be produced as, (a) products of deoxidation, which may be either oxides or combinations such as silicates, aluminates, etc.; (b) slag or refractory particles; (c) inclusions introduced in the metallic raw materials and deoxidizing agents used.

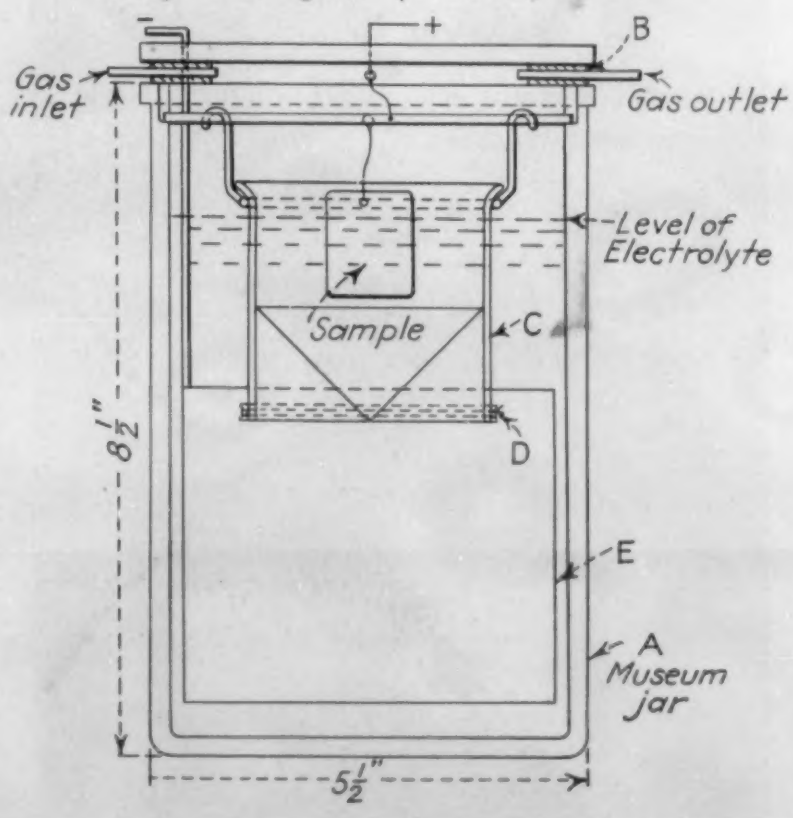
Ordinarily inclusions in steels are considered as objectionable, yet their presence in minute or sub-microscopic size probably has an important relationship to grain size and abnormality effects, hardenability, impact strength, etc. Moreover, the nature of the inclusions has an important bearing on their physical effects. Those of high melting point, for example, retain their shape during rolling, while inclusions of low melting point are elongated into "stringers" in which condition their detrimental effects are far more serious than the same amount of material in isolated and compact form. The degree of elongation on rolling depends upon the mineralogical composition of the inclusion phases.

An accurate knowledge of the nature and composition of inclusions is therefore extremely valuable in maintaining the desired close control of the properties of alloy steel. The usual methods of inclusion study, for example, metallographic inspection and chemical analysis of the oxides in steel, are insufficient in themselves to determine definitely the nature of the inclusion phases. The importance of having this information has therefore led to the development of a method of studying the problem utilizing and combining metallographic, chemical, petrographic and X-ray methods of study.

Metallographic examination alone has the great advantage of speed and observation of inclusions *in situ*, yet may lead to erroneous conclusions as to the chemical nature of the inclusions as well as being unfair as a whole, due to segregation of the non-metallic particles. This may be illustrated by the following calculation:

If the average inclusion is 0.001 in. in diameter (a large figure) all inclusions within a zone 0.001 in.

Fig. 1—Diagram of Electrolytic Cell.



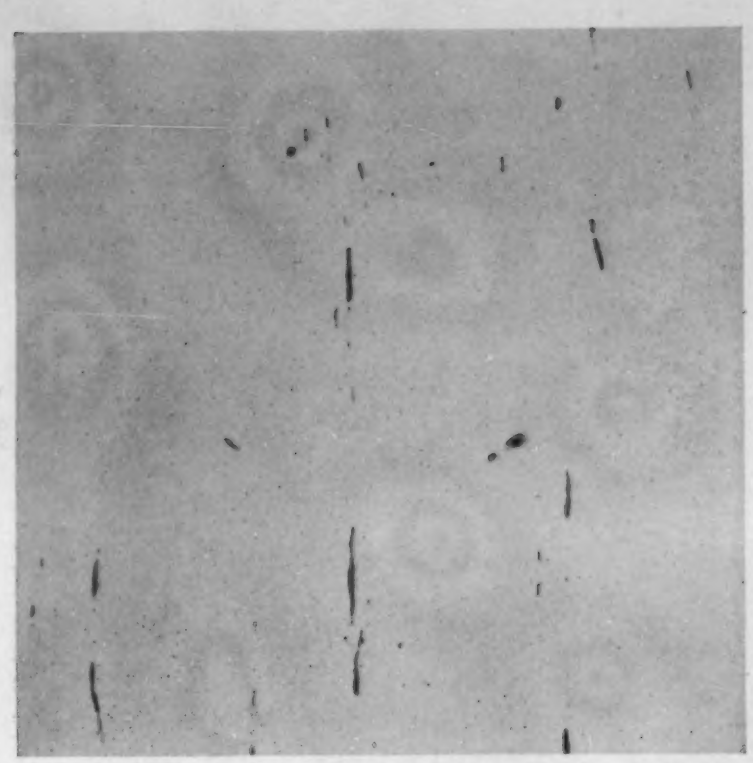


Fig. 2a—Metallographic Photomicrograph of Sample A Showing Elongated Inclusions. Magnification 200 X.

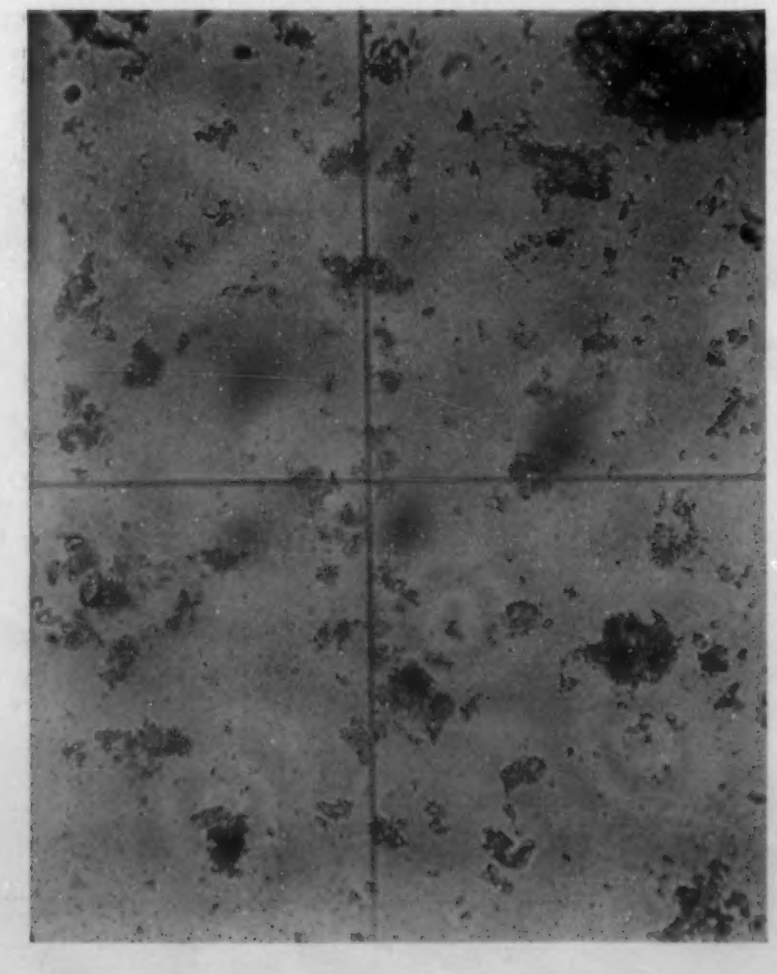
thick will be partially exposed on a polished surface. In the case of a surface ½ in. sq., the volume of steel being studied will be 0.00025 cu. in., weighing approximately 0.032 grams. In a chemical study of inclusions, however, one would use at least 20 grams for accurate sampling. Thus it appears that it would require several hundred polished surface observations to equal a single chemical analysis in fairness of sampling.

Chemical analysis avoids the effect of segregation to a considerable extent and permits accurate qualitative and quantitative analyses to be made. However, when used alone it does not show up the combinations or phases in which the oxides exist nor their manner of distribution in the steel.

Petrographic study of inclusions properly isolated by chemical means enables accurate determinations to be made of the actual phases or combinations of oxides representing each type of non-metallic inclusion present. In general, the methods of petrography comprise the identification of a non-metallic phase by the microscopic determination of its refractive index and other properties. Those inclusions difficult to study petrographically because of opacity or solid solution phase may be checked by means of X-ray diffraction powder photographs.

The present method of study consists, in general, of separation from a steel sample by suitable chemical means of the inclusion material free from contamination, and the determination of its total composition. A portion of the separated material is then studied petrographically to determine the phases composing the individual inclusions. The information thus obtained is checked by metallographic study, noting the inclusion distribution within the steel itself.

Fig. 2b—Photomicrograph of Petrographic Sample of Sample A. Magnification 200 X.



Sampling

To secure representative samples in our investigation, either entire cross section slices of rolled bars or "pie slice" sections, representing "middles" of ingots, were used. Previous work has indicated that drilling is unsatisfactory, fine drillings showing a much higher oxide content than coarse. All samples were therefore cut with a saw and filed with a clean file prior to study.

Method of Inclusion Separation

A rather extensive study of the various methods of inclusion analysis available in the literature was made with the result that with certain modifications the method[1] developed by F. W. Scott of Inland Steel Co. for the electrolytic separation of inclusions from plain carbon steel was found to be most suitable for application to most of the alloy steels produced at the Timken plant. This method employs the electrolytic decomposition of the sample as the anode in an electrolyte of magnesium iodide. Other electrolytes tried included Fitterer's solution, copper sulphate, various buffered solutions with tartrates and citrates present and potassium iodide solution. Only in the case of Scott's solution, however, was it possible to dissolve the steel without apparent contamination of the residue. We have modified the original Scott method to eliminate oxidation of iron salts by air during the electrolysis. This was accomplished by passing a neutral atmosphere over the sample and electrolyte as described below. We have also slightly modified the washing technique after electrolysis to eliminate attack on the inclusions during washing. The outline of the method at present being used by us is as follows:

The electrolyte is composed of a 7 per cent solution of magnesium iodide to which 3 grams of iodine per liter is added before each run. This is contained in a cell composed of a glass museum jar (A, Fig. 1) with a ground glass lid. Between the lid and jar is placed a ½ in. Bakelite spacer "B" through which several tubes are passed for inlet and outlet of neutral gas such as nitrogen and for electrode wires. The sample of about 30 to 60 grams is hung within the

beaker "C" whose bottom has been cut off and replaced by a sheet of hard filter paper "D" held in place by a rubber band. A sheet of quantitative filter paper folded conically is placed beneath the sample to catch any particles which might fall during the electrolysis. The level of the electrolyte is such as nearly to cover the sample, which is the anode of the cell. A cylinder of copper screen "E" in the outer cell is the cathode. In this cell the electrolysis is completed in the absence of oxygen and no iron salts or oxide are precipitated. The voltage used is held constant at 2 or 3 volts and about 2 or 3 days is required for the electrolysis to be complete.

After the electrolysis is complete the residue is removed and washed into a beaker with water, any non-electrolyzed sample being weighed and subtracted from the original sample weight.

Treatment of the Residue

The residue in the beaker is heated gently, filtered on a close paper and washed with hot water. It is then transferred to the original beaker by washing from the filter paper and treated with 50 cc. of 5 per cent sodium tartrate solution which is only slightly alkaline to phenolphthalein. This solution was substituted for the citrate recommended by Scott as it showed no reaction with manganese oxide, whereas the citrate seemed to dissolve some MnO. The residue is filtered and washed on the same paper and again transferred to the beaker and treated overnight with an alcoholic solution of iodine to decompose carbides. The amount of iodine used in this treatment (2 to 5 grams) varies with the carbides present, an excess of iodine being always provided. Except in the case of very low carbon steels, the treatment with alcoholic iodine is always given twice to assure complete carbide decomposition.

The residue is then filtered using the original paper and washed free from iodine with potassium iodide solution and hot water. It is then washed with the tartrate solution and with hot 5 per cent sodium carbonate solution to remove any gelatinous silica and finally with water. The residue is then ignited and analyzed by the usual chemical methods for Al_2O_3, SiO_2, MnO, FeO, etc.

For petrographic phase determinations an additional sample is prepared in the same way and the ignited residue, which is free from appreciable contamination, is studied.

Applicability of the Method to Alloy Steel

The method described above has been used on a large number of heats and specifications and appears to be entirely applicable to all types of steel except those containing both chromium and carbon in more than moderate percentages. Thus all plain carbon steel, nickel steels, low molybdenum steels, and the following chromium-containing steels, SAE 3115 and 3312, may be analyzed for inclusions by these methods. In the case of SAE 3135 steel, however, the carbon and chromium are present together to such a degree that there is some contamination of the residue with insoluble chromium carbide. In the case of SAE 52100 steel, the method is not suitable and we must resort

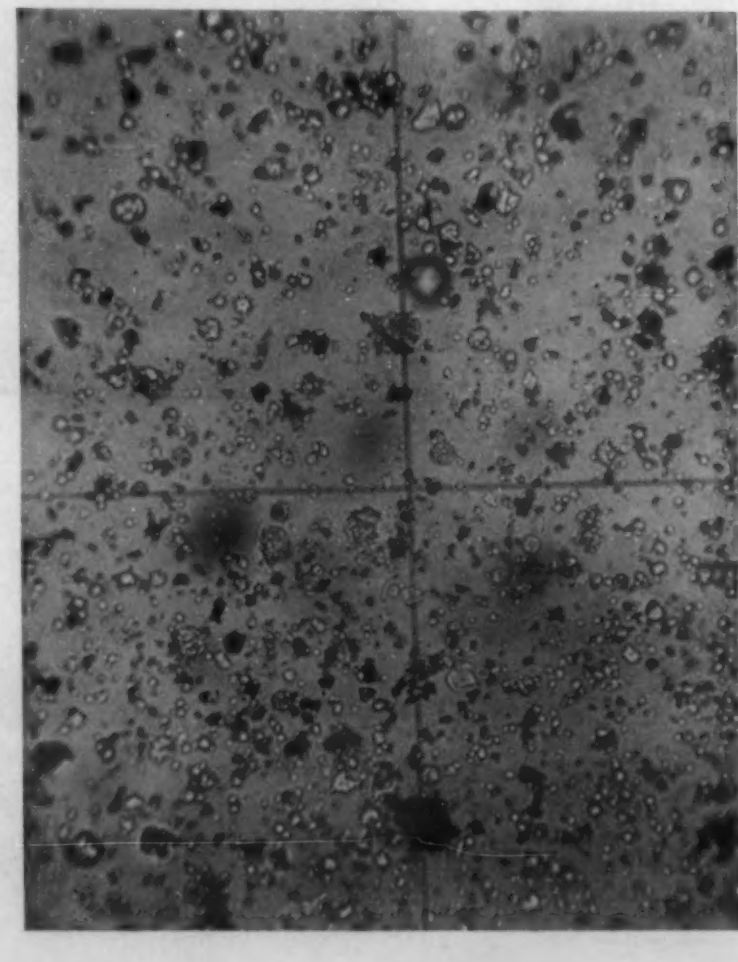
Fig. 3a—Metallographic Photomicrograph of Sample H Showing Non-Elongated Inclusions (Phase 6) Magnification 200 X.

to a dry decomposition of the metal in chlorine gas to study this type of steel.

Accuracy

The accuracy of the chemical analyses by the modified Scott method as used in this work is apparently very satisfactory. Oxides present may be checked on successive runs within very small limits. A set of eight samples used by the Bureau of Standards in a "Cooperative Study"[2] were analyzed by this method with results in almost every case within the limits chosen as "acceptable" by the correlators of the data.

Fig. 3b—Photomicrograph of Petrographic Sample of Sample H. Magnification 200 X.



Petrographic Analysis

The Table represents a summary of the chemical analyses and petrographic results found in eight heats of Timken alloy steels selected as representative of the conditions being studied. The phase numbers listed are described below the Table. It is seen that the heats are given in order of increasing Al_2O_3:SiO_2 ratio with regard to the inclusion analysis.

Table of a Summary of the Chemical Analyses and Petrographic Results on Eight Heats of Alloy Steel

Sample	Steel Type	Analysis of Inclusions, Per cent by weight				Mineralogical Phase, Approximate per cent present						
		Al_2O_3	SiO_2	MnO	FeO	1	2	3	4	5	6	7
A	1015	0.0049	0.0123	0.0036	0.0092	5	90	..	..	..	..	5
B	4615	0.0082	0.0061	0.0030	0.0109	..	..	80	..	..	10	10
C	4615	0.0107	0.0047	0.0033	0.0120	..	..	..	90	..	..	10
D	4620	0.0102	0.0031	0.0042	0.0112	10	15	10	..	..	..	65
E	1065+Mo.	0.0085	0.0023	0.0038	0.0127	15	..	..	..	25	..	60
F	4615	0.0163	0.0031	0.0029	0.0095	10	..	5	..	..	85	..
G	1065+Mo.	0.0159	0.0020	0.0043	0.0145	5	..	60	..	10	25	..
H	1065+Mo.	0.0210	0.0026	0.0036	0.0133	10	..	..	..	..	90	..

The phases listed in the above table are described as follows:

Phase 1—Quartz (SiO_2). This occurs as fairly large roughly broken pieces probably of exogenous nature. It is thought that the quartz represents entrained grog particles from firebrick and that because of the short exposure to high temperature the normal inversion did not occur.

Phase 2—A glass of 1.59 refractive index, yellow in appearance, found in inclusions of lower Al_2O_3 content. This phase probably contains FeO and MnO which raises its refractive index.

Phase 3—A glass phase of refractive index of 1.52-1.56. This is an aluminum silicate glass, possibly containing a little iron and manganese oxide. Probably the refractive index increases with the amount of Al_2O_3 present.

Phase 4—A glass of refractive index 1.53 thought to be of fireclay origin. This was found in one or two samples only.

Phase 5—A glass of 1.65-1.66 refractive index having a conchoidal fracture. This phase often contained corundum particles, so is probably of high alumina content.

Phase 6—Round or nearly round balls of corundum (Al_2O_3) probably containing a small amount of mullite ($3A_2O_3 ; 2SiO_2$) within them. These "balls" are obviously made up of a number of small individual particles of corundum sintered together to form a larger particle. Photomicrographs of this type inclusion are shown in Figs. 3a and 3b.

Phase 7—Pure corundum (Al_2O_3) present in individual particles not coalesced or sintered together as in Phase 6.

Two of these typical inclusion phases are illustrated in the accompanying photomicrographs. Phase 2 is typical of the sample "A" and is shown in Fig. 2a (x200) as it appears in the metallographic section. Being of low melting point, inclusions of this type invariably appear as stringers in samples taken from rolled bars. Fig 2b shows the appearance (x200) of this type of inclusion as observed petrographically after separation from the steel. The clumps of small particles are composed of the broken fragments of the stringers. That they are composed largely of SiO_2 is indicated by the analysis of sample "A" in the Table.

At the other end of the series are the inclusions of high Al_2O_3 content (Sample H). The photomicrographs shown in Fig. 3a and 3b are typical of Phase 6. Fig. 3a shows the non-elongated, nearly round inclusions observed metallographically. Fig. 3b shows the separated inclusions as observed petrographically. It will be seen in these figures that Phase 6 "ball type" inclusions predominate. A small amount of glassy material is likewise visible in Fig. 3b.

Application to Production Control

Knowing what the inclusions are, their constitution and properties, it is possible to apply this information to manufacturing practices in an effort to reduce the total number of inclusions, control their type, shape and distribution and study the effect of these changes on the various physical properties of the steels.

References

[1] F. W. Scott. "Extraction of Slag and Oxide Inclusions in Iron or Steel—Electrolytic Method." *Industrial and Engineering Chemistry, Anal. Ed.*, Vol. 4, Jan. 15, 1932, pages 121-125.

[2] J. G. Thompson, H. C. Vacher and H. A. Bright. "Cooperative Study of Methods for the Determination of Oxygen in Steel." *Metals Technology*, Vol. 3, Dec. 1936, T.P. 758, 44 pages.

A LETTER TO THE EDITOR

Not "Alm" for Aluminum in Germany

To the Editor: I am just as amused as you are about the germanizing of technical international words, of which you publish a few examples in your editorial of April, 1937. It is just as ridiculous as substituting "liberty cabbage" for sauerkraut. However, you should make a little correction in your editorial for the fact is that the German government prohibits this nonsensical germanization, as published in the magazine *Aluminium*, March, 1937. In the same magazine you will also find the reaction of German engineers on this subject. Therefore—to retain the well known reliability of METALS AND ALLOYS, you should make this correction.

1172 Plainfield Rd.,
Cleveland, Ohio

W. BONSACK

A CHUCKLE

Synthetic Metal from Ashes

To the Engineering Dept. (of a large company).

Enclosed is a piece of synthetic metal composed from ashes. Looks like silver.

Also synthetic gold. Sample of ore treated in nitrate and exposed to sun for visibilities of yellow particles average about ⅛ to ¼ oz. gold to oz. dirt—Secret Process. Silver or white metal for ½ to 1 oz. or in some cases 100% metal or, say, aluminum. Silver about 4% over yellow particles, a transparent substance that goes through glass, maybe radium.

Will pay 200% on $. Would you consider to make this a position or job in your presence, out of ashes, etc.?

Diffusion in Solid Metals—II

A CORRELATED ABSTRACT

by A. I. Krynitsky

Associate Metallurgist, National Bureau of Standards, Washington, D. C.
(Publication Approved by the Directors)

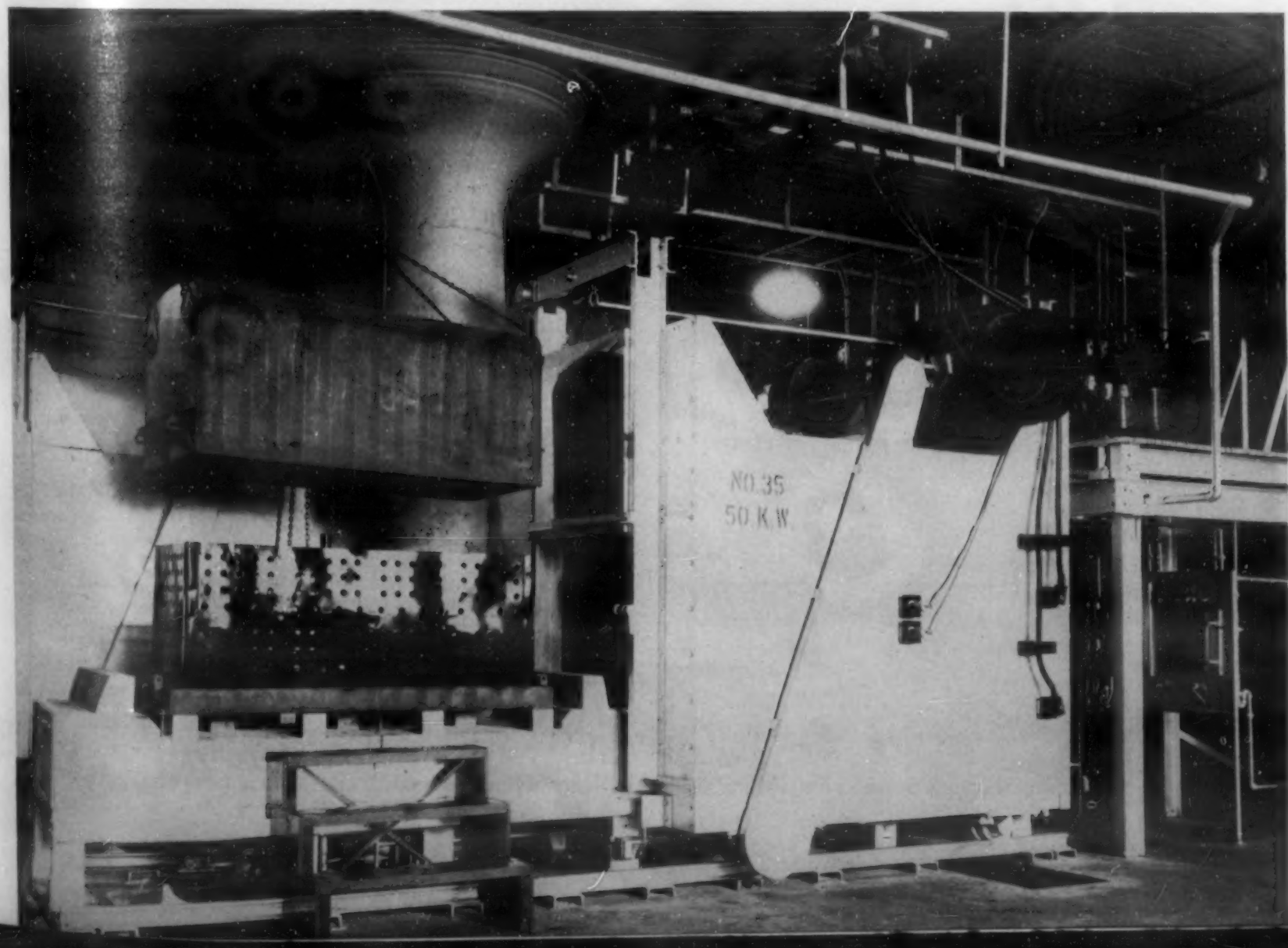
This is the second and last installment of this article. The first was published in the May issue.

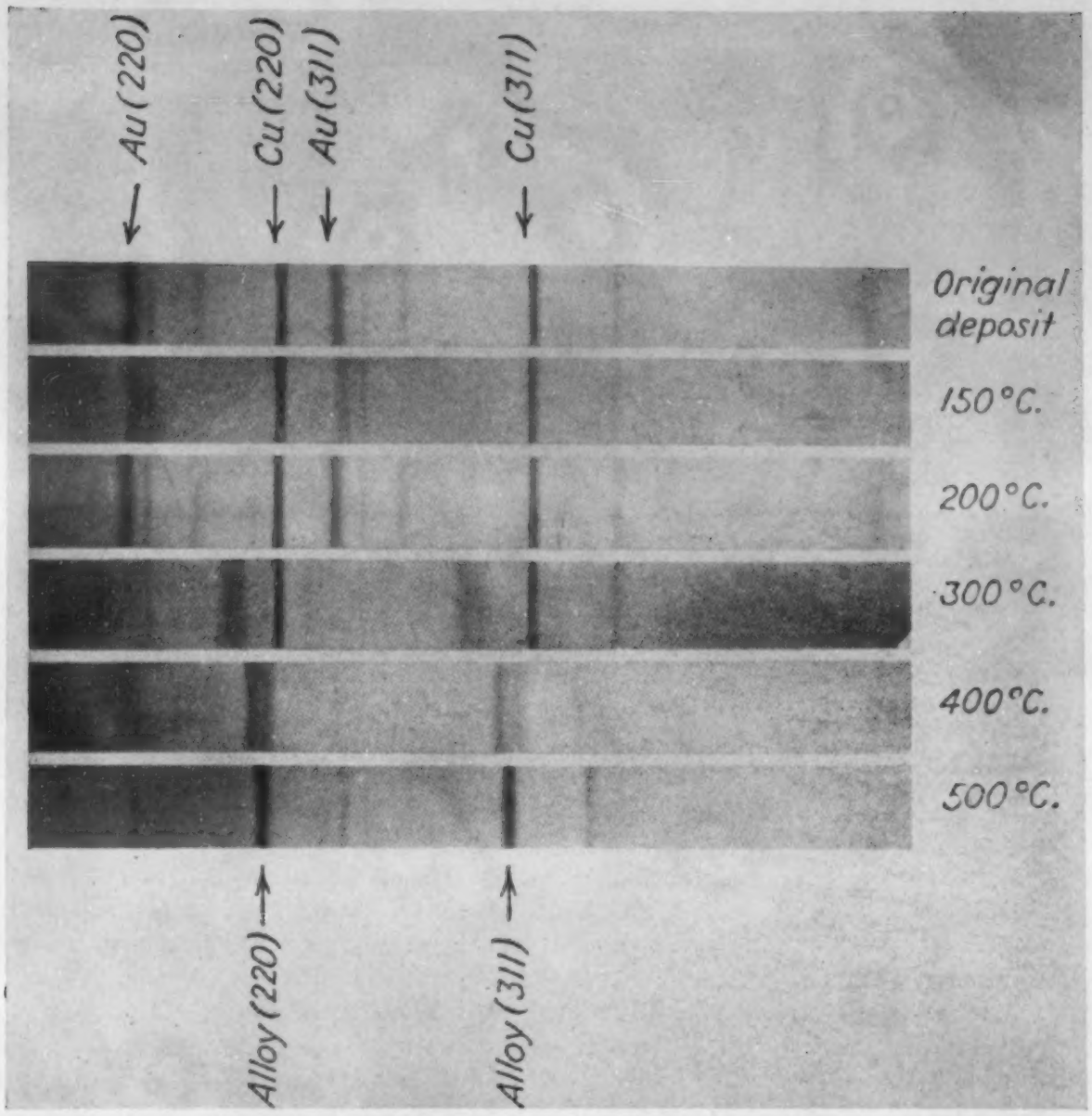
Diffusion Into Single Crystals and Self-Diffusion

The data relating to diffusion in single crystals are so scarce that practically no conclusions can be drawn in regard to this important problem. There is a belief[13], however, that no diffusion can take place with a closely packed lattice. It was shown[27] that carbon, iron, and molybdenum practically do not diffuse into single-crystal tungsten wire, whereas they diffuse readily into compressed tungsten powder. It was also shown[28] that diffusion of zinc into copper single-crystal is difficult, and that it depends on the vapor pressure of the zinc. On the other hand, when the single crystal is open-packed instead of close-packed, one may expect quite different results. For instance, Desch[13] believes that diffusion of atoms can take place without any disturbance in a quartz crystal, because in certain directions the quartz lattice is openly packed, and there are actual tunnels through it sufficiently large to admit a good many atoms.

An interesting supposition in regard to diffusion into single crystals was made by Belaiew[29], who called atten-

Nitriding is a Diffusion Process. The slow diffusion of nitrogen is responsible for the length of time required for nitriding. A semi-continuous electric furnace for nitriding is here shown. The furnace can be moved away from the retort to allow removal of the finished charge. (Courtesy: The Electric Furnace Co.)





X-ray Photogram Showing Diffusion Process in Copper-Gold System. The duplex sample was made by electrodepositing thin layers of the two metals alternately on top of one another to form a thin sheet. The sample was heated for 24 hrs. at each temperature. At 300 deg. C. a real change in line position has taken place. At 400 deg. C. mutual solubility has begun. At 500 deg. C. reasonably sharp lines of the homogeneous alloy are seen. V. G. Mooradian and John T. Norton. (Ref. 35.)

tion to the fact that under fatigue-stress and under some mechanical tests it is usually observed that the single crystals become polycrystalline, or that a certain mosaic structure is developed. Having this in mind, one may expect that under the influence of foreign atoms trying to get into the lattice and not being able to do so, changes on these lines may occur. One may also expect that the atoms are displaced from their equilibrium position so that the energy of loosening is lower than in a perfect crystal.

An extremely important contribution to the study of diffusion of two similar solid metals, one into another, so-called "auto-diffusion" or "self-diffusion," was made by Hevesy and his co-workers. The change of place of similar atoms among themselves cannot be detected in a pure metal. Therefore, the following method was employed. The diffusing atoms selected were those of the radioactive isotope of lead, thorium B, which should diffuse into lead at the same rate as ordinary lead. When two thin foils[30], one of ordinary lead, and the other with lead containing thorium B in homogeneous mixture, were pressed together in vacuo and heated, a diffusion of the active lead into the inactive one took place and the phenomena could be analyzed by means of the electroscope. The thickness of the inactive foil was chosen slightly greater than the range of the alpha particles to be measured. Therefore, no scintillations originating from the radioactive lead could be observed when investigating the inactive foil. But on heating the aggregate of the foils, a diffusion of the active lead into the inactive took place and the alpha particles, owing to the diffused atoms, or their successive products of disintegration, produced scintillations on the observing screen. By comparing the number of these scintillations with the number of scintillations produced by the active foil at the beginning of the experiment, the rate of self-diffusion in lead was determined.

In the case of a single crystal the method was somewhat modified to avoid stresses. Thorium B was collected in a hydrogen atmosphere on the surface of the single crystal of lead, and it was observed whether, after heating, a decrease in the number of scintillations could be noticed. In these experiments of Hevesy and Obrutsheva practically no self-diffusion was observed in the single crystal of lead, whereas this phenomenon took place in polycrystalline lead. On the other hand, it was found that the coefficient of diffusion of polinium into lead was the same both in the foil and in the single crystal. These observations led the authors to conclude that the atoms of polinium *"loosen the lattice of the individual lead crystal and a migration of atoms occurs through disturbed regions."*

When investigating the diffusion of two very similar metals like silver and gold, or thallium and lead, into each other, we can expect, the authors state, to find conditions not very far removed from those encountered in the case of self-diffusion. By using a foil of thallium and one of active lead they found that the rate of diffusion in such a case did not vary much from that of the self-diffusion in lead. It was later found by Seith and Keil[31] that there is no essential difference in the rate of self-diffusion in lead, whether the single crystal or polycrystalline lead are employed. It was shown, however, in their further investigation[32] that the rate of self-diffusion is greater in the lead distorted by mechanical work when compared with the rate

in the same metal recrystallized. Some of the results obtained in Hevesy's laboratory are given in Table 4.

Influence of lattice distortion on diffusion in solid metals.—

The principle advanced by Hevesy that some "loosening" of the lattice is necessary for atomic migration was accepted by many recent investigators. Seith and Laird[11] from their study on diffusion into lead of several elements (Table 4) came to the conclusion that, where the outer electron shells are very similar, i.e., the atoms are chemically closely alike (in this case Pb, Sn, Tl, Bi), there is little "loosening" of

Table 4—Some of the Results Obtained on Diffusion in Single-Crystal and Polycrystalline Lead in Hevesy's Laboratory.

Temperature Deg. C.	Diffusing elements	Diffusivity, sq. cm. per day	Investigators
280	Th B into Pb foil.....	1.5×10^{-6}	Hevesy and Obrutsheva [30]
310	Th B into Pb foil.....	5.7×10^{-6}	do
310	Po into Pb either single crystal or foil.....	1.3×10^{-5}	do
324	Th B into Pb foil.....	1.4×10^{-4}	do
324	Th B into Pb either single crystal or multi-crystalline	4.78×10^{-3}	Seith and Keil [31]
182	Th B in Pb either single crystal or multi-crystalline	4.12×10^{-8}	do
285	Sn into lead cylinder.....	1.4×10^{-5}	Seith and Laird [11]
	Tl into lead cylinder.....	2.7×10^{-5}	do
	Bi into lead cylinder.....	3.8×10^{-5}	do
	Ag into lead cylinder.....	0.79×10^{-2}	do

the lattice and therefore a small rate of diffusion should be expected; on the other hand, where the atoms differ considerably in these respects (Pb and Ag) the lattice is considerably loosened and diffusion is more rapid. They suggest that the atomic diameter, the type of lattice upon which the atoms crystallize and the nature of the outer shells of the atoms, play an important part. There is also some indication[32] that the element which penetrates the other is one whose atoms are closest together. Calculating the heat of lattice-loosening (Auflockerungswärme) Q for different elements and comparing their values with the coefficient of diffusion into lead (according to the above-mentioned relation, $D = Ae^{-Q/RT}$), at a given temperature, Seith and Keil[33] came to the conclusion that the smaller the heat of lattice-loosening of the entering element the greater is its coefficient of diffusion.

As may be seen in Tables 5 and 6, the heats of lattice-loosening of gold and silver are much smaller (or atomic mobility much greater than that of lead itself and, therefore, their coefficients of diffusion into lead are greater than that of the self-diffusion of lead into lead.

Table 5—Heats of Lattice-Loosening and Coefficients of Diffusion according to Seith & Keil[33]

Metals diffusing into Lead	Diffusivity at 285 deg. C., Sq. cm. per day	Heat of lattice loosening Q, cal. per mol.
Au	4×10^{-1}	14000
Ag	7.9×10^{-3}	15200
Cd	2.0×10^{-4}	~17000
Bi	3.8×10^{-5}	18600
Tl	2.7×10^{-5}	21000
Sn	1.4×10^{-5}	24000
Pb	6×10^{-6}	28000

Table 6—Diffusivity of lead, silver and gold into lead according to Seith and Keil[33]

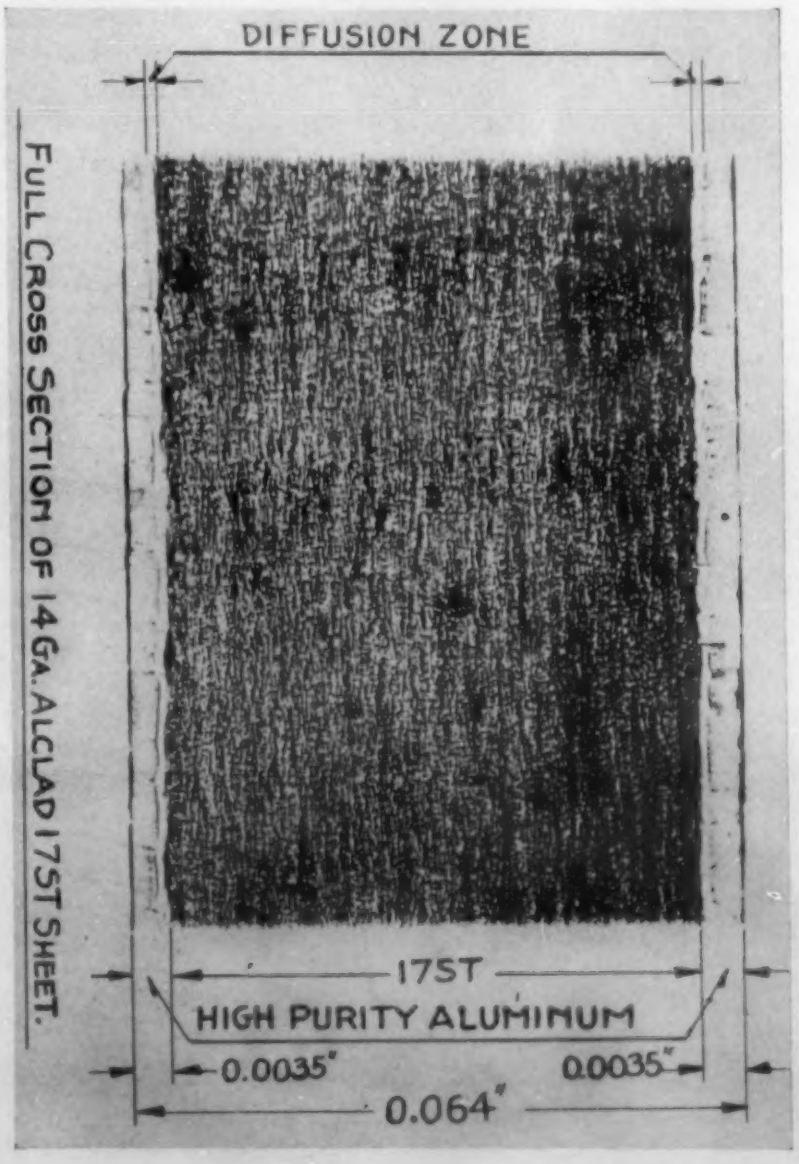
Temperature Deg. C.	Diffusivity in sq. cm. per day		
	Pb in Pb	Ag in Pb	Au in Pb
	Sq. cm. per day		
120	1.78×10^{-10}	.....	1.35×10^{-3}
160	4.68×10^{-9}	.....	7.08×10^{-3}
200	7.42×10^{-8}	6.6×10^{-4}	2.82×10^{-2}
240	7.58×10^{-7}	2.34×10^{-3}	8.9×10^{-2}
280	5.37×10^{-6}	7.08×10^{-3}	2.46×10^{-1}
320	3.14×10^{-5}	2.00×10^{-2}	5.62×10^{-1}

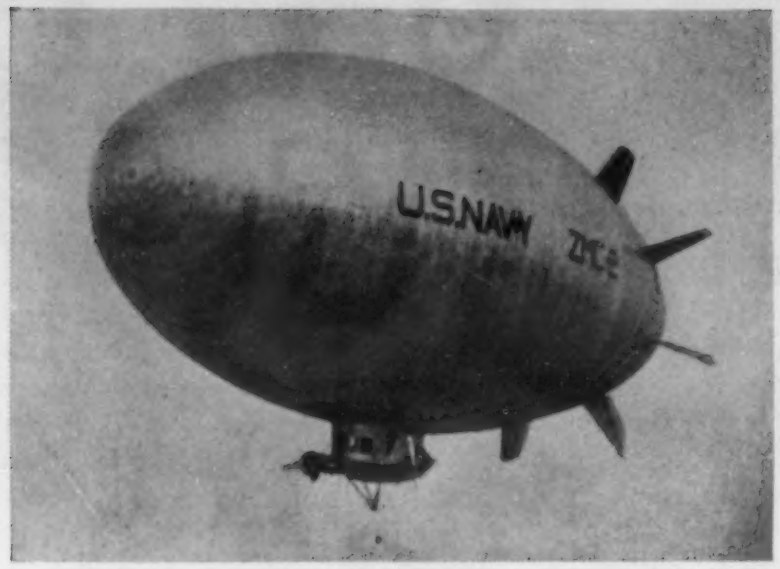
Only atoms containing a certain critical amount of kinetic (or potential?) energy, Langmuir states[34], are capable of making such interchanges (interchanges in position between neighboring atoms in the space lattice). The frequency of these changes of position and therefore the diffusion coefficient should thus be proportional to $e^{-Q_D/RT}$, where Q_D may be taken as the heat of diffusion or the critical energy (per gram-atom) involved in atomic interchanges.

To test whether a distortion of the lattice is necessary for atomic migration, the following experiments were undertaken by Mooradian and Norton[35]. Diffusion was produced by heating a duplex sample of the two metals at a series of different temperatures. Four different binary systems were examined: Copper-nickel, copper-gold, silver-gold, and nickel-cobalt. These all form continuous series of solid-solutions. The duplex sample was made by electrodepositing thin layers of the two metals alternately on top of one another to form a thin sheet. The relative amounts of the two metals were regulated so that X-ray diffraction lines of approximately equal intensity were obtained. The individual layers were so thin that the X-ray diffraction patterns were truly representative of the interior of the sample. It has been shown by Mooradian and Norton that in the original electrodeposits X-ray diffraction lines were rather broad.

In this particular case the presence of wide lines may indicate either fine grain size, lattice distortion, or variable composition from point to point. In view of the fact that there was no evidence of the presence of an extremely fine grain structure and that there was no variation in composition, it was assumed that the broad lines were due to lattice

Diffusion in Alclad. (Courtesy: Dix and Keller, Aluminum Co. of America Research Laboratories.)





The Only All-metal Airship in the World. Careful heat treatment was required to prevent excessive diffusion in the 0.0095 in. Alclad 17S-T skin sheet. (Courtesy: Aluminum Research Laboratories.)

distortion, as it is known that electrodeposits are under considerable mechanical strain. On the other hand, sharp lines indicate a uniform homogeneous structure free from strain.

The authors just mentioned showed the X-ray photograms obtained with copper-gold samples before heating and after heating in vacuo at 150, 200, 300, 400, and 500 deg. C. Both sets of lines were broad in the original deposit, the gold more so than the copper. At 150 deg. C. there was some improvement in the sharpness, and at 200 deg. C. still more. There was no change in line position up to this point. At 300 deg. C., however a real change had taken place. On one hand, the gold lines moved decidedly toward the corresponding copper lines and had become quite broad. On the other hand, the copper lines had not moved at all and had become even sharper. Thus the recovery temperature of the gold was somewhat above 300 deg. C. The copper had begun to be dissolved by the gold at 300 deg. C. but at this temperature none of the gold had been dissolved by the copper. At 400 deg. C. mutual solubility had begun and a broad line of the alloy only was visible. At 500 deg. C. reasonably sharp lines of the homogeneous alloy were seen.

The authors' conclusion was that the lattice distortion in the original samples is not an aid to diffusion. It may be even a hindrance and its removal is necessary before easy diffusion can take place. This conclusion, of course, does not explain why the diffusivity of similar atoms is very small as compared with that of atoms chemically different, as has been pointed out above.

General Remarks

IN VIEW of the wide contradictions in the results obtained and conclusions drawn by different investigators, it is doubtful whether a theory explaining all the facts observed can be formed at the present time.

The simple idea of interchange of places of adjacent atoms in the space lattice cannot explain the changes in volume and shape, which have been found[36], after diffusion in cast bismuth-antimony alloys which involve a strong coring effect. (See Table 7.)

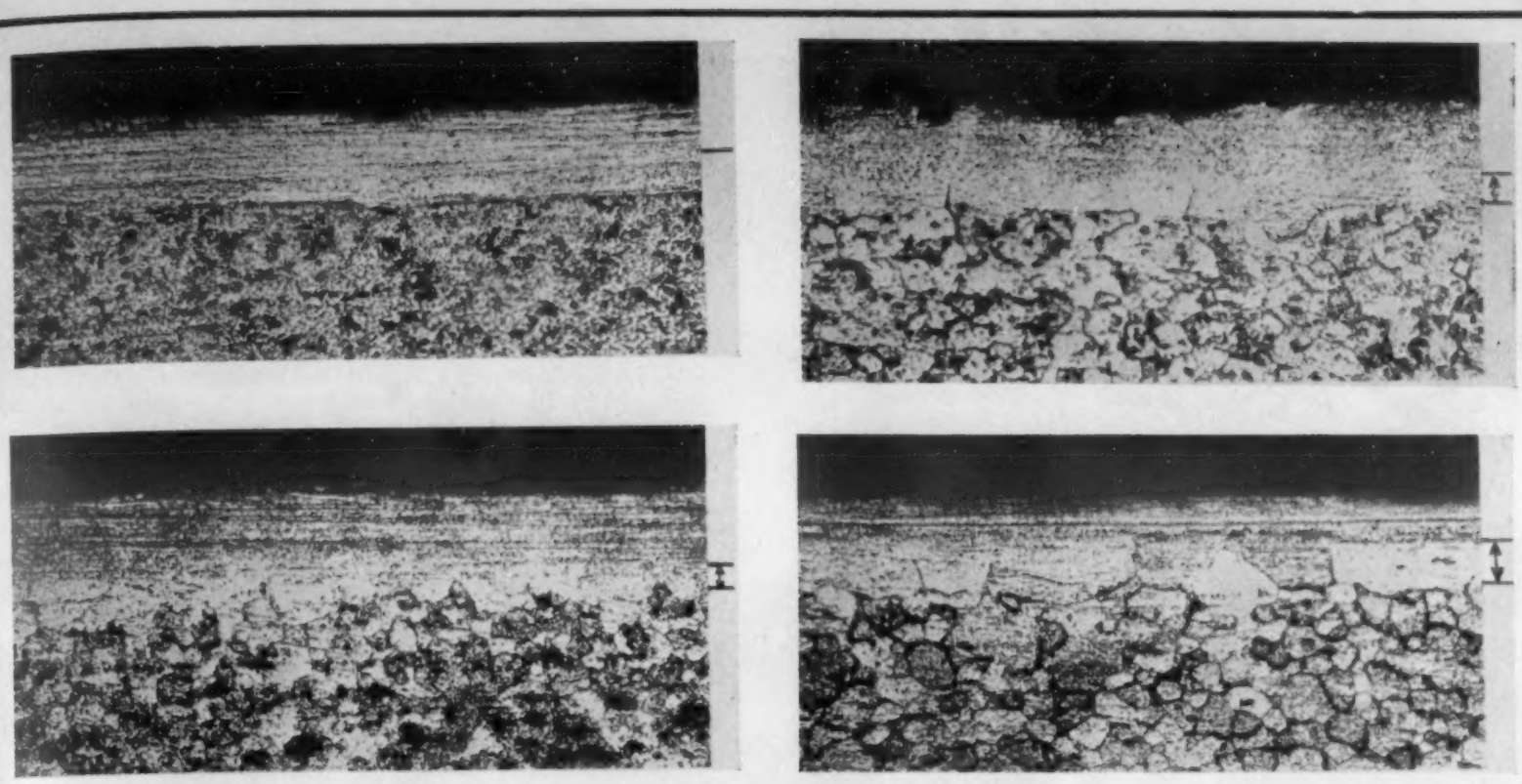
Table 7—Density Changes in Sb-Bi Alloys (25 per cent Sb) after Different Annealings, according to Masing.[36]

Mode of solidification	Temperature of Annealing, Deg. C.	Density: Before Annealing	Annealed 10 hrs.	Annealed 48 hrs.	Annealed 72 hrs.
Cast in mold.....	300	8.822	7.919	7.498	7.254
Cast in mold.....	260	8.829	8.491	8.443	8.150
Frozen in crucible..	300	8.824	8.362	8.423	8.353
Frozen in crucible..	260	9.022	8.977	8.889	8.231
Cast in mold.....	300 in absence of air	8.818	8.143	....	....

Rosenhain's "Slip Diffusion" Theory

The observations show, Rosenhain states, that diffusion in solid crystals is confined to bodies of very simple struc-

The Latest Airway Luxury: A Douglas "Sleeper" Plane. But diffusion in the Alclad covering sheet must be controlled to prevent color contrasts in the unpainted surfaces. (Courtesy: Aluminum Research Laboratories.)



Progress of Diffusion in Duplex Material of The Alclad Type. Micrographs, x 250, show diffusion of copper in "Allautal" sheet (Al + 4% Cu + 2% Si) not heated and heated for 7, 12 and 25 mins. at 500 deg. C. The thickness of the pure aluminum coating was 0.05 mm. A. Burkhardt and G. Sachs. (Ref. 18.)

ture, such as the metals having a cubic or hexagonal symmetry, and to a lesser extent to such simple lattices as those of alkali halides. Bodies with a more complex lattice structure, such as the metals having a tetragonal symmetry, the majority of intermetallic compounds, and particularly crystals of inorganic salts, cannot be brought to show the phenomena of diffusion except at temperatures so near their melting points that local incipient fusion may be supposed to play a part.

Having in view these considerations Rosenhain[1] proposed his theory of diffusion which closely links that process with the mechanism of slip. In the case of slip under mechanical stresses, movement takes place at a plane of the crystal lattice because only in that way can the stresses be relieved. The motive power or stress in the case of diffusion is believed to be set up by the local disturbance of the crystal lattice caused by the presence of a "stranger" or solute atom. This stress, however, can be relieved by the movement of a single row of atoms instead of the displacement of a whole block or sheet, and it is by such movement of rows of atoms along all the principal directions of the crystal that diffusion can alone take place. There was, however, a serious difficulty that a very long row of atoms might have to be set in motion before any movement at all could occur, and it has been doubted whether the local stresses caused by the lattice disturbances around the solute atom would be sufficient to overcome the initial resistance to movement of so long a row.

However, according to recent views of crystal structure, crystals are not a homogeneous array of atoms strictly marshalled on a single lattice, but consist of crystal blocks, which are not built together with complete and perfect regularity, but differ very slightly in orientation, and leave, where they meet, something in the nature of looseness of structure or even interstices. According to Rosenhain these interstices or "loose spaces" between these crystal blocks or units probably are the real channels of diffusion. This theory presupposes that the advance takes place by slip brought about by distortion, and that diffusion should occur only in plastic crystals. According to Desch[13] however, the plasticity is not essential and the geometrical considerations mainly determine diffusion. As the packing in a crystalline solid becomes looser, Desch states, migration becomes easier, an example being seen in the zeolites, the packing in which is so open as to allow large ions such as potassium and barium, and water molecules to migrate freely.

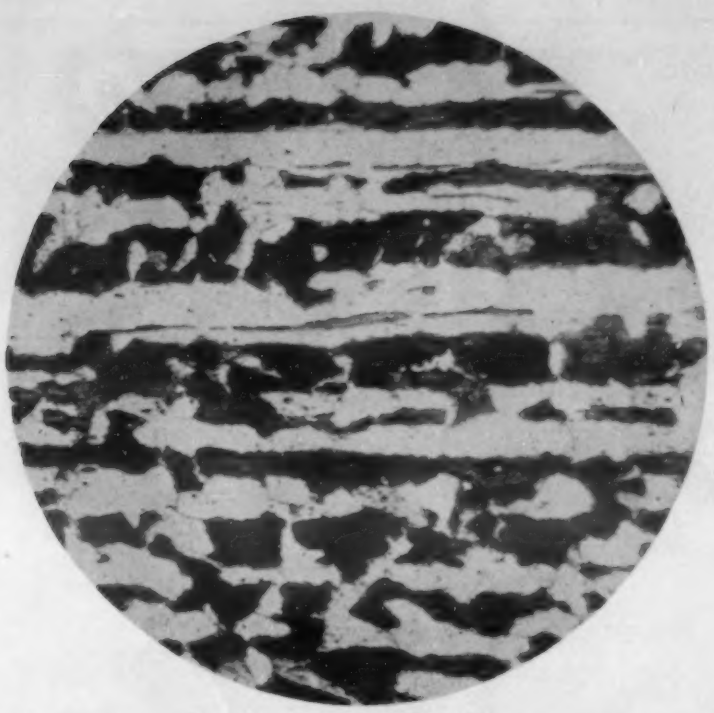
The process of "cementation" (in general) is not discussed because this subject is beyond the scope of this abstract. However, the reader may be referred to such important papers on this subject as those by Guillet[37], [38], and Laissus[39].

Two Valuable Papers

After the present abstract had been completed, two extremely valuable papers on diffusion in solid metals were presented to the American Institute of Mining and Metallurgical Engineers, one of the Annual Institute of Metals Lecture by R. F. Mehl[42], and the other a paper by Hertha R. Freche[43].

The investigation of Freche was carried out on Alclad material. The magnesium and silicon in the high-purity alloy core diffused into the high-purity aluminum coating. The rates of diffusion of magnesium and silicon from the alloy core into the aluminum coating were determined from the quantitative spectographic data obtained from a series of 0.003-in. (0.0076-cm.) steps machined in the Alclad coating. In addition, it was determined how the simultaneous presence of silicon affected the rate of diffusion of magnesium into aluminum.

The alloys were chill-cast in the form of 1 lb. ingots, 2 by 9 by 10 cm., and the high-purity aluminum coating was rolled on to both sides of the alloy ingots after proper surface preparation of the metals. The resulting material was rolled down to the form of a slab about 12.7 cm. wide and 0.63 cm. thick. The average thickness of coating on either



Banded Structure in Steel. (Courtesy: Prof. Bradley Stoughton, Lehigh University, Bethlehem, Pa.)

When the ingot contains crystals of variable phosphorus content, the rolled steel shows bands resulting from the deformation of these crystals. On account of the slow diffusion of phosphorus, such a structure is difficult to homogenize.

side of the slab corresponded to about 0.063 cm. The specimens were heat-treated (heated and quenched) at temperatures of 450 and 510 deg. C. for different periods of time, and examined.

Fick's second law of diffusion:

$$\left(\frac{dc}{dt}\right)_x = D\left(\frac{d^2c}{dx^2}\right)_t,$$

was used to express the relation of the concentration C of diffusing metal to the time t and the depth of diffusion X, D being the coefficient of diffusion.

The experimental data appear to indicate that the diffusion of magnesium from the binary aluminum-magnesium alloy, and the diffusion of silicon from the binary aluminum-silicon alloy, into their respective high-purity aluminum coatings are of the same order of magnitude. The simultaneous presence of magnesium and silicon in the ratio of Mg_2Si seems to decrease the amount of diffused silicon. The magnesium and silicon tend to diffuse into the aluminum coating in the approximate ratio of Mg_2Si if the alloy core is an aluminum-magnesium silicide alloy. However, if the alloy core contains excess of silicon and magnesium silicide, the diffusion of magnesium in aluminum is greatly diminished, with the result that the Alclad coating contains an excess of silicon. This excess silicon necessarily will have an effect on the corrosion resistance of the Alclad material.

The paper of Mehl is too comprehensive to be briefly abstracted. The following account, however, includes most of the outstanding points. According to Mehl the best data available on the rate of diffusion in solid metals are in good accord with the previously mentioned general diffusion equation[8] proposed by Dushman and Langmuir:

$$D = \frac{Q}{Nh} d^2 e^{-Q/RT},$$

where Q is the heat of diffusion, N is Avogadro's number, h is Planck's constant, d is the interatomic distance ("jump distance"). The applicability of this expression is not limited to substitutional solid solutions, but extends as well to the interstitial solid solution (carbon in gamma iron). However, it cannot be applied to the systems of non-cubic metals.

The relation between melting point and D and Q are of a particular interest. In considering the great number of data Mehl concludes that:

> (1) The rate of self-diffusion at a given temperature is the lower the higher the melting point of a metal.
> (2) In a series of alloys with a common base metal, such as the lead alloys described above, the rate of diffusion is the greater the higher the melting point of the diffusing metal.
> (3) In a binary system the rate of diffusion is the greater in the lower-melting metal.

The effect of third elements upon the rate of diffusion offers other interesting possibilities. Mehl writes that inasmuch as third elements when present in sufficient quantity will greatly modify the lattice characteristics, such as the dimensions of the unit cell, an effect from this source might be readily predicted. He points out that Bramley and his co-workers[40] found many surprising effects, among which may be mentioned that oxygen decreases the rate of diffusion of carbon in gamma iron, as does sulphur, that carbon decreases the rate of diffusion of phosphorus, and that oxygen increases the rate of diffusion of nitrogen. A supposition is advanced that some phenomena observed may have been caused by the effect of third elements on grain size.

Three types of diffusion—volume, grain boundary, and surface diffusion—are discussed.

Surface mobility appears in many systems, and in many cases the phenomena can most safely be described as a spreading rather than a diffusion. The surface film of several elements on tungsten obey the diffusion laws and possess temperature coefficients of rates of diffusion quite analogous to those for volume diffusion. This process is conceived as a two-dimensional diffusion. The study of the relationship between the three types of diffusion of thorium in tungsten reveals that the rate of diffusion increases in the sequence—volume, boundary, surface.

In discussing the possible effect of crystallographic direction upon the rate of diffusion, the author concludes that the rate of diffusion in cubic crystals is independent of the direction measured and that the only example available of diffusion anisotropy in metal crystals is that of the results obtained on the self-diffusion in bismuth, which show that the rate of diffusion at 269 deg. C. perpendicular to the rhombohedral axis is greater than that parallel to the same axis by a factor of approximately one million.

The conception of thermal lattice-loosening has been extended by several writers to include mechanical loosening originating in cold work and also loosening associated with lattice imperfections and mosaics. In view of the fact that distortion produces a less dense structure and less symmetrical force field, the diffusion should be more rapid in distorted metals than in undistorted metals, but it is difficult to demonstrate the effect, for the rate of recovery from the effects of strain is much more rapid than the rate of measurable diffusion.

In the discussion of the correlation between the rates of age-hardening in alloys and rates of diffusion, reference is made to the work of Seltz and Hone at the Carnegie Institute of Technology in 1933, who showed that the initial

rates of precipitation of the gamma phase from the thermal solid solution of Ag in Al (as measured by change in electrical resistance) varied exponentially with temperature and could be expressed by an equation of the Dushman and Langmuir type. These results suggest that the rate of diffusion is the controlling factor in determining the rate of aging.

Suggestion is also made by Mehl that the preferential precipitation of an aging constituent at the grain boundaries may be associated with an increased rate of diffusion at the grain boundary, and that this effect may be lacking in systems in which grain boundary diffusion is no more rapid than intragranular diffusion.

It is further stated that "if a compound is to precipitate from a solvent, such as Mg_2Si from Al, it is evident either that the two atoms must diffuse at the proper relative rates to give the compound, whatever the normal rate of diffusion of each may be, as Mrs. Freche suggests, or that the rate of diffusion of the more slowly diffusing metal controls the rate of precipitation; it is also at least possible in such cases that some phase other than the predicted compound may appear first on precipitation, as was shown by Mehl, Barrett and Rhines for the system Al-Mg_2Si[41]."

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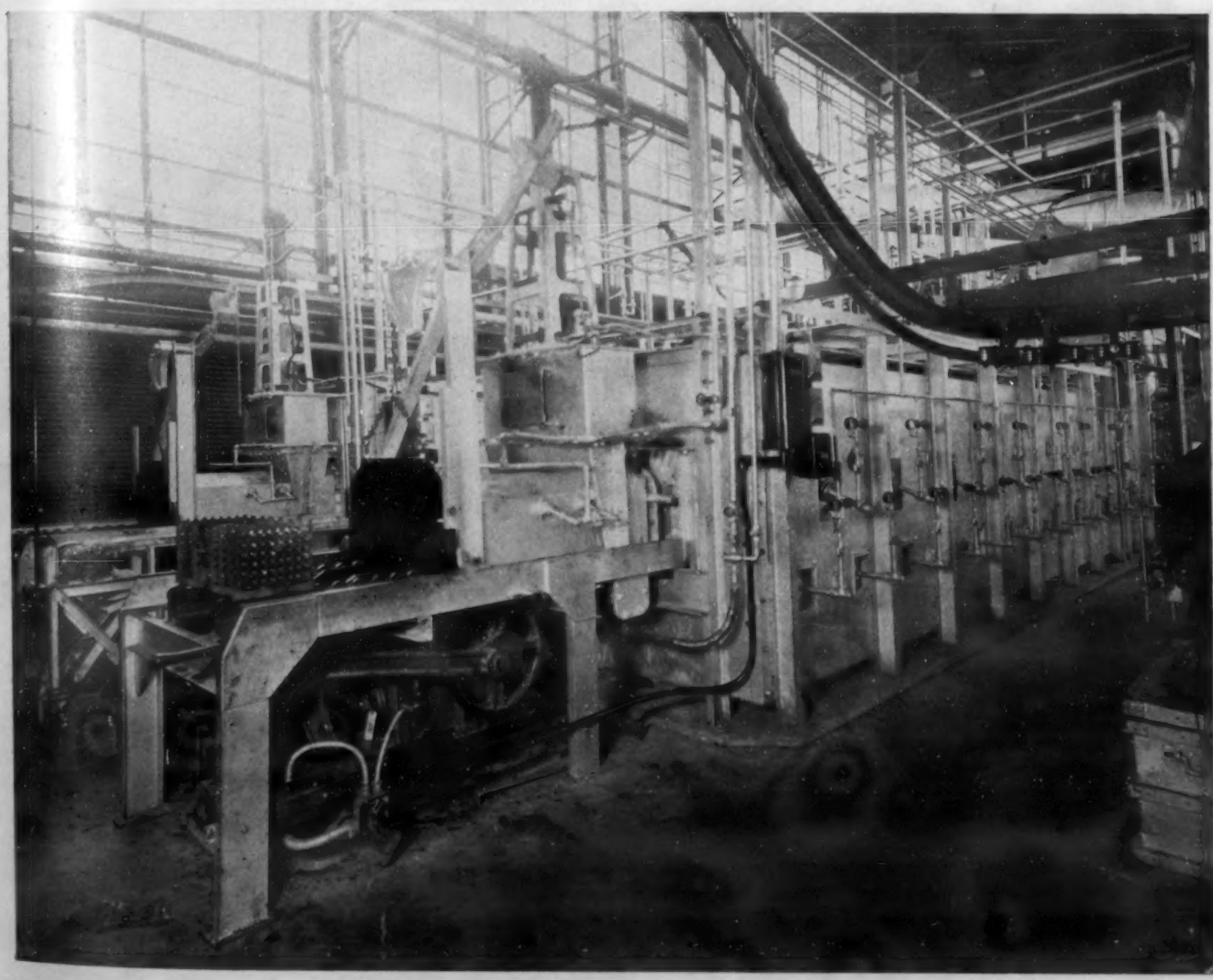
Two Continuous Gas-Carburizing Furnaces. (Courtesy: Surface Combustion Corp., Toledo, Ohio.)



Courtesy: Bethlehem Steel Co.

Rolling Steel Sheets

ATMOSPHERE FROM HOT CHARCOAL FOR

ANNEALING COPPER

by H. D. Holler

Research Engineer, Westinghouse Research Laboratories, East Pittsburgh, Pa.

THE BRIGHT ANNEALING OF COPPER requires a furnace atmosphere free from traces of oxygen and sulphur to prevent tarnishing; and also one having a low content of reducing gases (hydrogen or carbon monoxide) to prevent embrittlement. Such an atmosphere may be obtained by passing air through a charcoal furnace.

The dry gas producer, i.e., apparatus for production of a fuel gas from carbon in the absence of intentionally added moisture, has been discussed many years ago (e.g., Kovenaar A., "Combustion in the Gas Producer and the Blast Furnace," 1924, Crosby Lockwood & Son) while the C, CO, CO_2 equilibrium was discussed by Boudouard back in 1901 (*Ann. Chim. Phys.*, 1901, page 5) and by many other investigators since.

Johannsen and von Wachenfeldt (Jernkontorets Annaler, June, 1929, p. 141-179) described the use of a dry producer using charcoal for manufacture of a protective gas for annealing steel. Cone (METALS AND ALLOYS, February, 1937, pages 33-37) has mentioned the use of charcoal producer gas, made at a high temperature, for protection of molten oxygen-free, high-conductivity copper.

Because of the apparent simplicity of the dry producer method, its possible advantages seem worth some experimental study.

Composition of the Atmosphere

When dry air is passed through a granular mass of charcoal at furnace temperature, the resulting gas mixture consists principally of nitrogen, carbon dioxide and carbon monoxide, the proportions of these gases depending upon the temperature of the charcoal. Since any moisture present reacts with the carbon to form hydrogen and carbon monoxide, the amount of hydrogen in the annealing gas may be controlled by regulating the moisture content of the charcoal and the humidity of the incoming air.

The following percentages of carbon dioxide and of carbon monoxide in equilibrium with carbon at different temperatures (nitrogen by difference), as given in Table I, were taken from Johansson and von Wachenfeldt.

For annealing copper, a satisfactory atmosphere seemed available at the lower temperatures given in Table I, inasmuch as the prevention of embrittlement requires a low content of the reducing gas, carbon monoxide. Since small traces of sulphur in the annealing atmosphere are frequently a cause of tarnish when city gas is used, the use of charcoal should offer a distinct advantage in this respect inasmuch as it may be obtained free from sulphur. In a properly designed furnace, traces of oxygen in sufficient concentration to cause tarnishing may be eliminated. Furthermore, since the hydrogen may be maintained below that concentration where embrittlement occurs, by controlling the amount of moisture, a non-tarnishing and non-embrittling atmosphere seemed readily obtainable.

Table I.—Percentages of CO_2 and CO in Equilibrium with C at Different Temperatures

Temperature, Deg. C.	Percentage		
	CO_2	CO	N_2
900	0.35	33.75	65.90
850	0.75	33.20	66.03
800	1.60	31.70	66.70
750	3.45	28.65	67.90
700	6.60	23.45	69.95
650	10.65	16.80	72.55
600	14.55	10.40	75.05
550	17.55	5.40	77.05
500	19.35	2.45	78.20

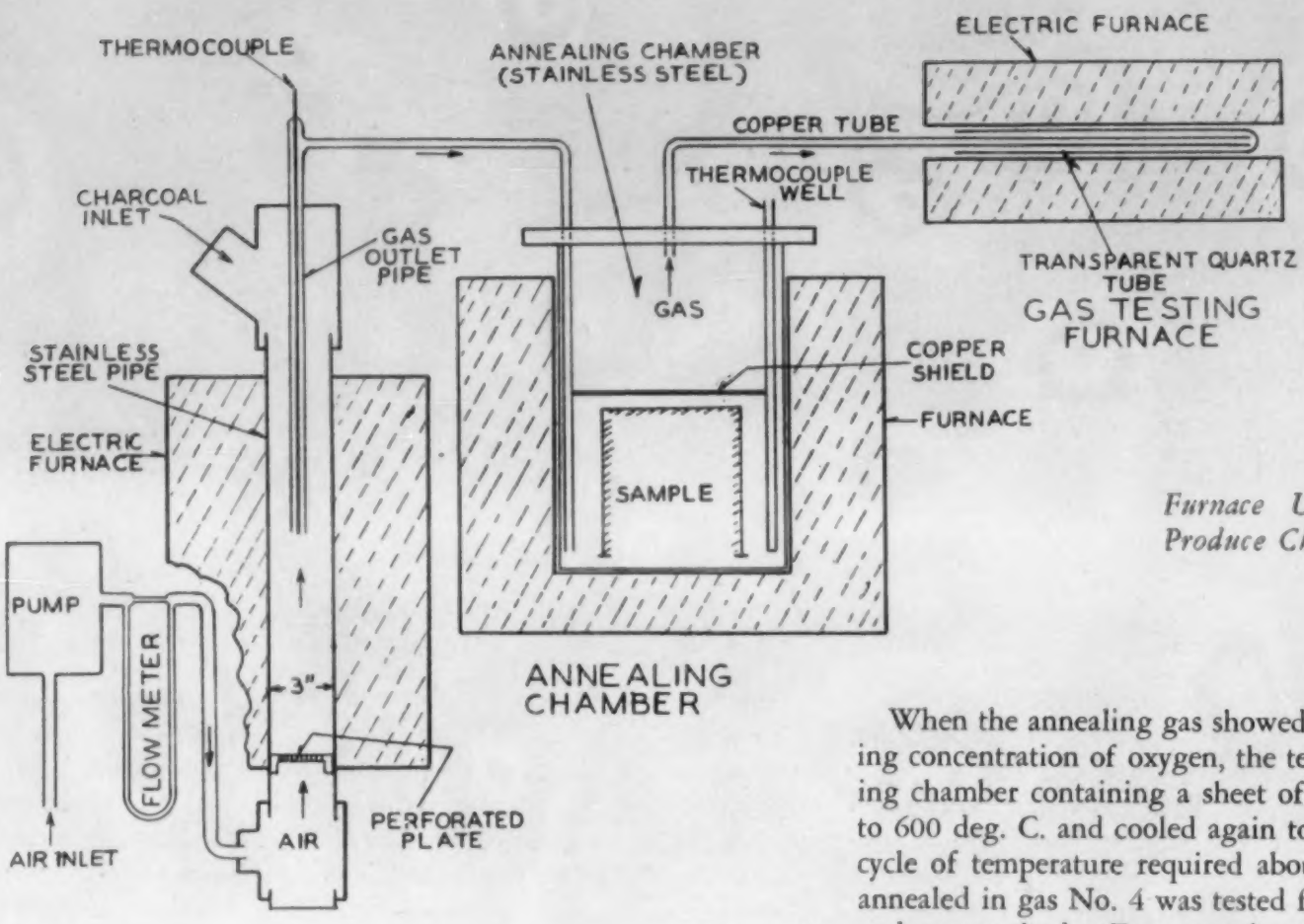
Experimental Furnace Used

For producing experimentally a small supply of charcoal gas, a producer (see illustration) was made by using a 3-in. stainless steel pipe, 24 in. long, inserted in a tubular furnace of the same length, in a vertical position and electrically heated. A perforated plate in the lower end of the pipe supported the wood charcoal granules having dimensions from about 1/4 in. to 3/4 in. At the upper end of the pipe a Y was attached, one branch serving as a feed door for adding charcoal and the other branch, as outlet for gas. The air was introduced through the perforated plate at the bottom. The gas outlet was a 1-in. pipe extending down to the middle of the furnace. The outlet pipe therefore led the gas off from the hottest section of the furnace and the thermocouple was located there.

The chamber in which the copper was annealed consisted of a stainless steel cylinder 12 in. deep and 7 in. in diameter. It was provided with a circular steel plate cover, carrying gas inlet and outlet tubes and an asbestos gasket. A thermocouple tube extended to the bottom of the chamber. The annealing chamber was lowered into an electric furnace which provided temperatures up to 600 deg. C. The annealing gas was led directly from the charcoal furnace to the annealing chamber without any further treatment.

Gases Obtained from Furnace

The analyses in Table II show the compositions of gas mixtures obtained with this furnace, the temperatures being



Furnace Used Experimentally to Produce Charcoal Gas.

that of the thermocouple where the gas left the charcoal.

Table II.—Analyses and Temperatures of Experimental Gases

Sample No.	1	2	3	4
Temperature, deg. C.	800	700	650	550
Temperature, deg. F.	1472	1292	1202	1022
Percentage by Volume				
Carbon dioxide	8.2	13.1	13.4	17.1
Carbon monoxide	18.9	10.3	10.0	3.7
Hydrogen	11.4	3.4	2.0	1.2
Nitrogen (by difference)	61.5	73.1	74.6	77.9

The percentages of carbon dioxide and monoxide obtained in Table II were not correlated with temperature as in Table I because of the presence of considerable hydrogen.

Sample No. 1 in Table II was prepared from undried charcoal, which contained 2.4 per cent water. This accounted for about two thirds of the hydrogen, the remainder coming from the humidity of the air. Samples Nos. 2, 3 and 4 were prepared from dry charcoal, dried by filling the furnace with charcoal and allowing it to stand over night at furnace temperature before using. The hydrogen in the last three samples, therefore, came from moisture in the air.

The temperature of the charcoal furnace was successively lowered until the percentage of reducing gases ($H_2 + CO$) was below that necessary to change the color of the copper. Samples Nos. 1, 2 and 3 produced a marked color-change, while the effect of No. 4 was barely perceptible.

Prior to making the annealing tests, it was necessary to determine when the oxygen in the annealing chamber had been diminished to a non-tarnishing concentration. This was done by leading the gas from the chamber into a transparent quartz tube supported in an electric furnace whose temperature could be easily varied. The gas was passed through a ¼-in. copper tube directly from annealing chamber into the quartz tube. When a copper strip showed no tarnish, as the temperature of the quartz tube was lowered through the tarnishing zone, the chamber was considered free from oxygen and the annealing test then carried out.

When the annealing gas showed freedom from a tarnishing concentration of oxygen, the temperature of the annealing chamber containing a sheet of 5-mil copper was raised to 600 deg. C. and cooled again to room temperature. This cycle of temperature required about 1½ hrs. The copper annealed in gas No. 4 was tested for elongation by the ball and cup method. Four samples of metal gave the following elongations with a 1-in. ball: 0.365, 0.370, 0.360 and 0.365 in. Similar readings on the un-annealed sheet averaged 0.350 in. On the bases of these results, the gas was satisfactory insofar as freedom from color-change and embrittlement is concerned.

No study was made of the charcoal furnace with a view to supplying information for the design of one for commercial use. A rate of 5 cu. ft. of air per hour was used for the above tests. Twice this rate was used several times without passing sufficient oxygen to cause tarnishing.

The charcoal used in the above tests was obtained from the Cliff Dow Chemical Co., Marquette, Mich. Before receiving this material, a bag of "Tennessee Oak" charcoal was purchased in Pittsburgh. Both materials seemed equally satisfactory.

Quantity of Charcoal Involved

The amount of charcoal required per unit volume of annealing gas depends upon the proportion of carbon dioxide and monoxide which is determined by the temperature of the charcoal. In the complete combustion of charcoal in air to CO_2, according to the equation

$$C + O_2 + 3.78\ N_2 = CO_2 + 3.78\ N_2$$

1000 cu. ft. of annealing gas at 740 mm. and 25 deg. C. (29.1 in. mercury and 77 deg. F.) would require 6.2 lbs. of carbon.

If only CO be produced according to the equation

$$2C + O_2 + 3.78\ N_2 = 2\ CO + 3.78\ N_2$$

1000 cu. ft. of annealing gas under the above conditions would require 10.4 lbs. of carbon. Since wood charcoal is almost entirely carbon (the sample used in these tests contained 2.4% water and 1.4% ash) and a small percentage of CO is desirable for annealing copper, the amount of charcoal required would be slightly more than 6.2 lbs. per 1000 cu. ft. At the market price for charcoal, the cost of the annealing gas would be moderate in view of the situation that the cost of water, oxygen, and sulphur removal is eliminated.

Metallurgical and Commerce News

BY THE EDITORS

Stresses in Welded Joints

A very interesting and instructive address on "Stresses in Welded Joints and How to Eliminate Them", was delivered before a joint meeting of the New York local sections of the American Welding Society and the American Society for Metals recently. The speaker was Everett Chapman, president of Lukenweld, Inc., Coatesville, Pa., regarded as an authority on welding and cutting of metals.

As a discusser of such a complicated subject, Mr. Chapman was unique in his frankness. He did not claim that welding is a cure for many or all evils. He frankly pointed out many of its possible weaknesses particularly those involving stresses. For many of them he presented a remedy, among which was the avoidance of a design or a construction which could result at any point in setting up stresses. He pointed out, by means of slides of photoelastic curves, the possible damaging effects of stresses and particularly stress concentrations. One point which he frequently emphasized was that too frequently troubles and failures are due to the mistakes of the designing engineer.

Some of the types of steels used in the operations of his company were discussed. He dealt with both rimming and killed steels and the relative effects of composition and segregation of these on the welding of the plates. Alloy steels were frequently brought into the picture. In reply to a question, Mr. Chapman said that his company is using principally manganese-molybdenum steels as well as some Cromansil. The Mn-Mo type used is one with about —.90 to 1 per cent Mn and 0.40 to 0.50 per cent Mo. In all cases, the speaker said, it is his aim to keep the carbon not over 0.18 per cent.

Spiegeleisen Consumption at Record Volume

Very little, if any, data are available—and almost nothing has been published—as to the consumption of spiegeleisen by American users. This information can, however, be arrived at by an analysis of separate data available. The method is as follows:

Total production of ferromanganese and spiegeleisen is reported each year by the American Iron and Steel Institute. The leading trade papers collect each month the production data for ferromanganese and their figures are usually correct. The imports of spiegeleisen are reported monthly by the Bureau of Foreign & Domestic Commerce. Subtracting the trade paper yearly total for the ferromanganese from the Institute's total for the ferroalloy and spiegeleisen output gives the latter's production. Add to this the imports and one has the approximate total consumption of spiegeleisen each year. The result of such an analysis is as follows in gross tons.

	Output	Imports	Consumption
1929	140,850	13,800	154,650
1930	85,850	13,400	99,200
1932	36,300	8,300	44,600
1933	25,900	26,300	52,200
1935	104,100	54,000	158,100
1936	140,390	52,000	192,390

Thus the 1936 consumption of spiegeleisen at approximately 192,390 tons exceeded that of 1929, the boom year by over 37,700 tons. The expansion since 1932 in consumption is also a reflection of the expanding recovery.

Sodium Fluoride in Ingot Molds

The practice of adding sodium fluoride to ingot molds in open-hearth practice was one of the subjects discussed at the annual conferences of the Open-Hearth Committee of the A.I.M. and M.E., at Birmingham this spring. A general discussion brought out the fact that such additions are advantageous. The practice has been in use by several operators for several years.

It was stated that, for rimming steel ingots, the proper amount of sodium fluoride to add is 2 oz. per ton for lower carbon heats with 3 oz. per ton for the higher carbons. It should be thrown in when 2 to 3 in. of molten steel is in the mold. It was agreed that the action is more mechanical than chemical as indicated by the roaring sound and the intense sodium flame. An advantage from its use is reported to come from the violent momentary mechanical action, according to the testimony of operating men. One operator testified that the use of sodium fluoride moved the primary blow holes in from the surface and that such holes are cleaner and smaller.

As to the effect of sodium fluoride on the surface of the ingot, it was common opinion that there is very little and, if any, only a slight improvement. The treated ingot needs possibly less chipping.

Large Increase in Sponge Iron Imports

With 1,176 tons of sponge iron imported into the United States to April 1, the total for 1937 has risen to a record figure. The record thus far in 1937 compared to previous years is as follows in gross tons:

Year	Total Imports	Tons per Month
1931	216	17.5
1932	185	15.4
1933	619	51.0
1934	898	75.0
1935	1460	107.0
1936	1950	162.0
1937 (3 mos.)	1455	485.0

It will be noticed that, at 485 tons a month for the first three months of this year, the imports are many times the volume in 1936 and that the trend has been steadily upward right through the depression.

The majority, if not all, of these imports of sponge iron come from Sweden. It is a high grade product, made by a special process developed in that country. Almost none is made commercially in this country, although there are numerous patents for its production.

The chief use of sponge iron is as a raw material in the production of high grade steels. It is claimed that, when this iron is mixed with the charge in electric furnaces, the quality of the steel is much improved. This same material in the form of powdered iron is also used as a raw material in powder metallurgy—the production of various alloys by mixing the powdered metals and subjecting them to great pressure and heat. There are many interesting applications of the powdered product, particularly by one or two large automobile manufacturers.

Good Steel from High Sulphur Iron Ore

At the general luncheon during the annual conference of the Open-Hearth Committee of the A.I.M. and M.E. at Birmingham, Ala., in April, the principal speaker was Earl C. Smith, chief metallurgist, Republic Steel Corp. His address was a most interesting recital of his experience visiting steel plants in several European countries.

Discussing the rather unique blast furnace operations at Corby, England, where low grade ore, high in sulphur, is being converted into good steel, mainly for pipe, Mr. Smith is quoted as having said:

Blast furnaces at Corby, England, are using 29 per cent iron ore containing 0.20 to 0.80 per cent sulphur, and are desulphurizing the molten pig iron in the ladle and in basic mixers with soda ash, hydrogen and steam. The quantity of soda ash used is about 1 per cent of the iron. The pig iron made by this process is high grade. The production cost is about $9 per ton or possibly a little less. A German plant uses liquid soda ash for the same purpose, lowering the sulphur from 0.08 to 0.04 per cent.

Ferromanganese Output Heavy

With the sharp upturn in steel production this year, there has come a decided increase in the output of ferromanganese by American blast furnaces. The total for the first four months has been 101,810 gross tons or 25,450 tons per month. Compared with 1936 and with previous years the authoritative record is as follows in gross tons:

Year	Total Output	Tons per Month
1913	119,493	9,960
1918 (war)	333,027	27,750
1929	335,799	27,820
1930	276,500	23,040
1931	212,115	17,673
1932	57,342	4,780
1933	136,852	11,400
1934	124,190	10,350
1935	185,173	15,431
1936	254,728	21,227
1937 (4 mos.)	101,810	25,450

Thus at over 25,450 tons per month this year to May, the ferromanganese production is nearly 20 per cent higher than in 1936. It is substantially in excess of the volume in 1930 of 23,040 tons each month and is over five times the volume of only 4,780 tons monthly at the low point of the depression in 1932. It is not far from the record American production of 27,820 tons per month in 1929.

That the output of this important steel making alloy is a measure of the rate of steel ingot output is clearly demonstrated by these data. The ferromanganese production is a barometer of the trend of the American steel industry.

New Russian Manganese Ore Mine

It is estimated that, as a result of development work at the manganese mine at Mazul in the Achinsk region of Russia, where 12 deep shafts have been sunk, the reserves of manganese ore of merchantable grade run to 10,000,000 metric tons. In 6 of the shafts sunk ore bodies have been tapped which are estimated to run 45 per cent Mn, according to *Foreign Metals and Minerals* of the Bureau of Foreign and Domestic Commerce. In one shaft the thickness ran as high as 75 meters.

South Africa to Make Ferromanganese

Production of ferromanganese is to be undertaken in the near future at the Newcastle, Natal works of the Union Steel Corp. of South Africa, according to Commercial Attache Samuel H. Day at Johannesburg. The profitable export of locally produced ferromanganese has been made probable by higher prices recently obtained, coupled with the fact that South African manganese ore is now in regular production. The Newcastle plant, closed for 5 years, will not produce pig iron as heretofore but will confine its operations to ferromanganese.

World Output of Steel in 1936 Exceeds All Records— Total Pig Iron Large

There has been published estimates of the world production of pig iron and steel ingots and castings by two authorities—*The Iron Age* and *Steel*—in their annual review issues. The totals as published are as follows in thousands of gross tons—compared with 1935:

	1935	*1936*
Pig Iron:		
Iron Age	72,770	89,434
Steel	72,713	89,615
Average	72,741	89,524
Steel Ingots and Castings		
Iron Age	95,850	119,550
Steel	97,613	123,640
Average	96,731	121,595

Taking the average of these two estimates as representing, probably quite closely, the approximate world production, we find the following:

	1935	*1936*
Pig Iron	72,741	89,594
Steel	96,731	121,595

Thus at 121,595,000 gross tons, the world steel output in 1936 was about 25.5 per cent larger than in 1935. With pig iron totalling approximately 89,524,000 tons in 1936, the increase over 1935 was approximately 23 per cent.

Compared with previous years the world total for steel was the largest ever recorded while that for pig iron was the largest since 1929.

Output of American Spiegeleisen

Not since 1926 has the American Iron and Steel Institute published the actual data of the American production of spiegeleisen. Since then only the combined tonnage of ferromanganese and spiegeleisen has been made public.

It is possible, however, to arrive at the approximate amount of spiegeleisen produced each year by deducting from the total tonnage of the two ferroalloys the quantity of ferromanganese as published by *The Iron Age* and *Steel* which collect these statistics each month. Adopting such a method the following table is arrived at for the yearly production of spiegeleisen in approximate gross tons:

1928	82,250
1929	140,850
1930	85,856
1931	22,700
1932	36,300
1933	25,900
1934	61,600
1935	104,100
1936	140,390

Regarding these figures as reliably accurate, the 1936 output of spiegeleisen at over 140,300 gross tons was nearly equal to the boom year of 1929 when it was 140,850 tons. The recovery in steel operations, since the 1931 to 1933 period, is also clearly reflected by the expansion in output.

The largest output reported by the American Iron and Steel Institute from 1918 to 1926 inclusive was 161,147 tons in 1918—a war year—with 75,730 tons in 1926 as a normal year.

There is a larger use in recent years for spiegeleisen as a deoxidizer in open-hearth practice.

World's Longest Rails

The longest rails in the world—120 ft.—are claimed by *Industrial Britain* to have been laid on the London & North Eastern Railroad Co.'s main line in England; 100 tons were used. It is believed these are the longest rails ever produced in one piece in any part of the world.

METALS USED IN THE

Development of Power Cables

by W. H. Bassett, Jr.

Manager, Metallurgical Development,
Anaconda Wire & Cable Co., Hastings-on-Hudson, N. Y.

NO DISCUSSION OF THE METALS used in power cables would be complete without reviewing briefly the history of copper production in the United States. Native or metallic copper was known in this country long before the earliest visits of European explorers. The American Indians found the "red metal" in the Northern peninsula of Michigan.

In 1845, three years after S.F.B. Morse installed the first submarine communication cable in New York harbor, the total production of copper in this country was 100 tons. The metal was obtained from five states along the Eastern seaboard, Vermont, Pennsylvania, Virginia, North Carolina, and Georgia. Ninety years later we find that the production of primary refined copper amounted to 611,000 tons, according to the U. S. Bureau of Mines. The five states producing the largest tonnage were Arizona, Utah, Montana, Michigan, and Nevada, the important sources of copper having moved to the west and none of the original states being included in the group of important producers.

While the production in 1935 shows a material increase over the last three years, it is still materially below the peak production of 1,437,000 tons, in 1929, also U. S. Bur. of Mines data.

The first commercial production of fire refined Lake copper was started in 1850. Lake copper was the standard of the American industry for over 50 yrs., because of the uniform high quality of the Lake Superior ores. It was not until 1883 that the first electrolytic copper was produced by the Balbach Smelting & Refining Co. This was 23 years after the first successful dynamos were produced, which are so essential in furnishing cheap power for the electrolysis of the copper.

The first commercial arc light systems, established in 1877; Edison's incandescent lamp, invented in 1879; and Stanley's constant pressure alternating current system of distribution, invented in 1886, all increased the demand for copper which is the best industrially available conductor of electricity. In spite of the rapid increase in the use of the metal, it was not until 1911 that the first industry standard for copper wirebars was published by the American Society for Testing Materials. Because Lake copper was still a very important factor in the American market, the specification was revised two years later and two specifications were written, one for Lake copper, and the other for electrolytic copper. These standard specifications have remained essentially the same for the last 25 years. In 1927, the specifications were again revised to include the physical dimensions of the wirebars, slightly increase the metal content (copper plus silver 99.900% min.) and conductivity (99.33% min. I.A.C.S.) and permit the use of high resistance Lake copper when required by the purchaser.

As stated before, for 50 years fire refined Lake copper was the standard of the electrical industry. The tests conducted by W. H. Bassett in 1903 and 1904, which showed that the physical properties of electrolytic copper were equal or superior to the fire refined Lake copper, were used in a legal action to justify the delivery of electrolytic copper. From that time electrolytic copper has led the field.

The importance of the electrolytic process is readily illustrated by the fact that during the past 25 years over 90 per cent of the production has been in this class of material, the present figure being about 94 per cent.

The smelting and electrolytic refining methods developed by the American producers have reduced the impurities in

Copper Wire Bars As Received from the Refinery

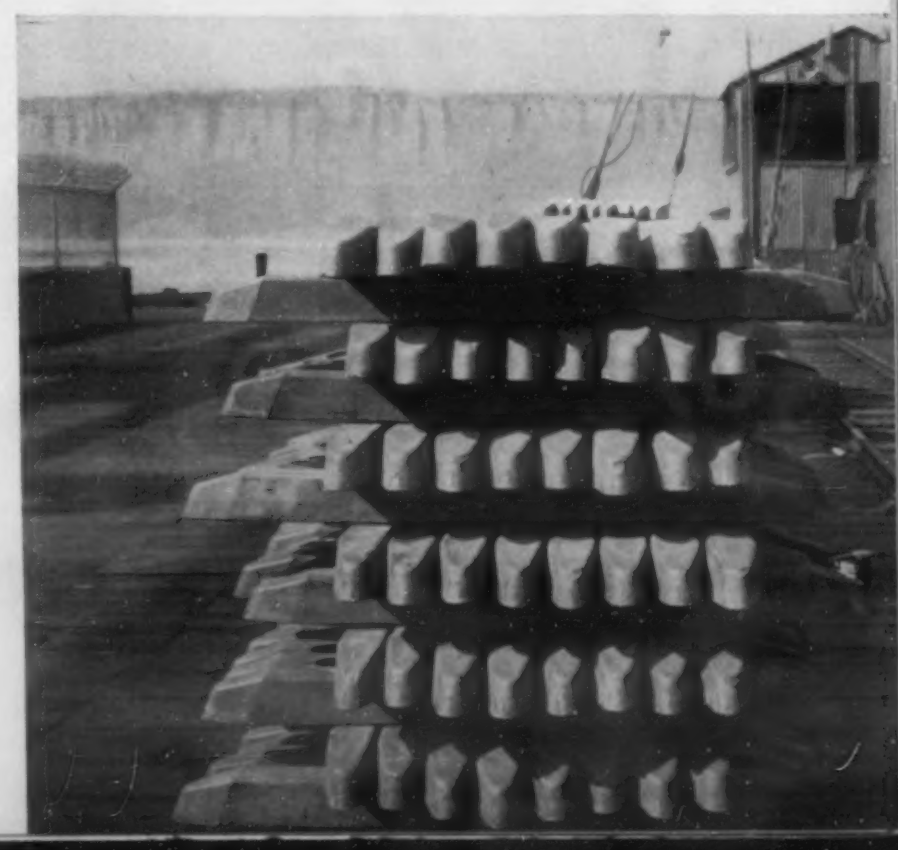


Table I.—Investigation of Quality of 0.102 in. Diameter Copper Wire Produced from Four Types of Wirebar with Different Wire Drawing Machines

		Average Breaking Strength, Pounds	Average Elongation in 60 in., Per Cent	Average Bends 0.202 in. Rad., Number	Average Twists in 6 in.,	Bend Flatback Checking				
						None	Slight	Med.	Pron.	Bad
				CONTINUOUS DRAWING MACHINE TYPE A						
44A	OFHC	583	1.02	10.4	86.3	10	..	..	..	..
43A	End poured	591	1.16	6.1	78.8	10	..	..	..	..
42A	Scalped	592	1.28	5.2	68.8	10	..	..	..	..
41A	Electrolytic	593	1.19	5.0	44.5	..	..	1	9	..
40A	Electrolytic	593	1.19	5.0	47.6	..	..	2	5	3
				CONTINUOUS DRAWING MACHINE TYPE B						
18B	OFHC	565	1.03	11.5	91.7	10	..	..	..	..
17B	End poured	568	1.03	7.9	82.0	10	..	..	..	..
19B	Scalped	571	1.07	6.0	62.1	9	1	..	..	..
20B	Electrolytic	566	1.06	6.6	41.5	5	2	3	..	..
21B	Electrolytic	561	1.03	6.6	45.3	3	1	3	3	..

copper to a minimum, with the result that the electrolytic copper has been very uniform in quality. The tabulation of a large number of tests of the leading brands of electrolytic copper show an average purity of 99.930 per cent copper plus silver, and an average conductivity of 100.75 per cent I.A.C.S.

In 1932, the United States Metals Refining Co., a subsidiary of the American Metal Co., placed on the market a grade of copper known as OFHC oxygen-free high-conductivity copper. This material was developed to meet the demands of the transatlantic communication cable manufacturers who required a copper wire that could be annealed in hydrogen without becoming brittle. As a result of this development, we now have five grades of wirebars on the American market:

1. Fire refined Lake copper
2. Electrolytic copper
3. Scalped electrolytic copper
4. End poured or VC electrolytic
5. Oxygen-free types.

Copper Wire from Wire Bars

Exhaustive tests in various laboratories have shown that there is no appreciable difference in the tensile strength and elongation of wire manufactured from the five grades of wirebars. The Westinghouse Electric & Mfg. Co. has published results which indicate that the end poured oxygen-free copper has greater resistance to bending and torsional stresses. Table I gives typical results in testing 0.102-in. diameter hard copper wire manufactured under identical conditions from four types of wirebars.

In making the bend test, if the surface of the wire having the "set" (area of oxide concentration) is on the outside of the bend so that it is severely stressed, the wire will crack or "check." If the wire is rotated 180 deg. so that the "set" is on the inside of the bend, there will be no cracking or checking of the outer surface of the wire. As shown in the publications of the American Smelting & Refining Co. and the American Metal Co., structural differences can be noted in the wires manufactured from scalped and end poured oxygen-free bars, when the material is examined under the microscope. The three types referred to above are readily identified by the absence of the areas of oxide concentration.

Except in the case of vertical riser cables, where medium hard and hard wires are required, soft copper wires are universally used in the construction of power cables. Soft wire manufactured from the various types of wirebars shows no appreciable differences in physical properties. In fact most mechanical tests fail to identify the difference in soft wires and it is usually necessary to resort to microscopic examinations in order to determine the type of wirebar used in producing the soft conductors. In the case of flat wire used in the construction of hollow conductor cables and for armature windings, the producers' publications indicate that the scalped and end-poured oxygen-free bars produce material which has greater resistance to edgewise bending and twisting.

During the past five years most American power cable manufacturers have discontinued the use of steel binder tape. In its place, non-magnetic copper, commercial bronze (90 copper, 10 zinc), and copper-silicon-manganese alloys (such as Everdur) have come into common use. The latter named alloys of the silicon bronze type are especially desirable, due to the fact that they have a strength equal to that of mild steel.

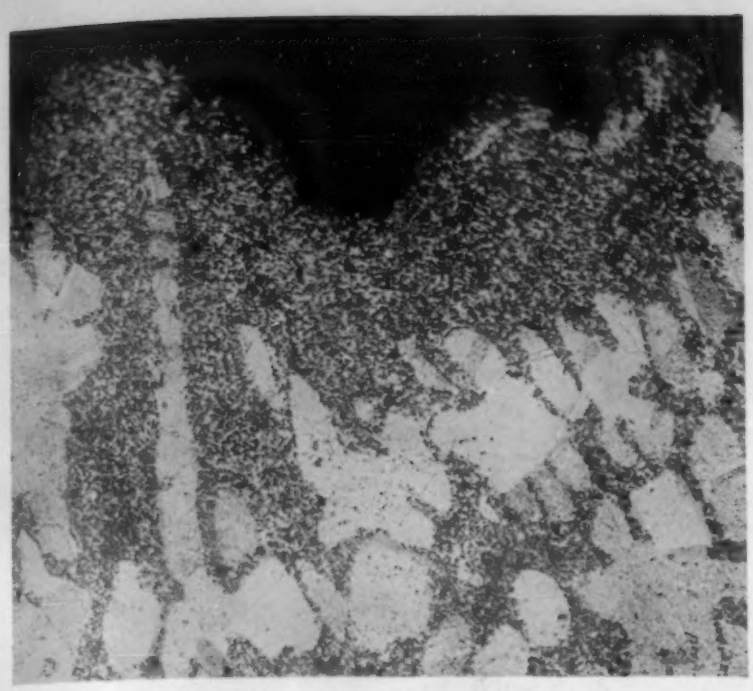
Lead for Sheathing Cable

It was natural that electrical engineers should use lead as a protective covering for their insulated cables, inasmuch

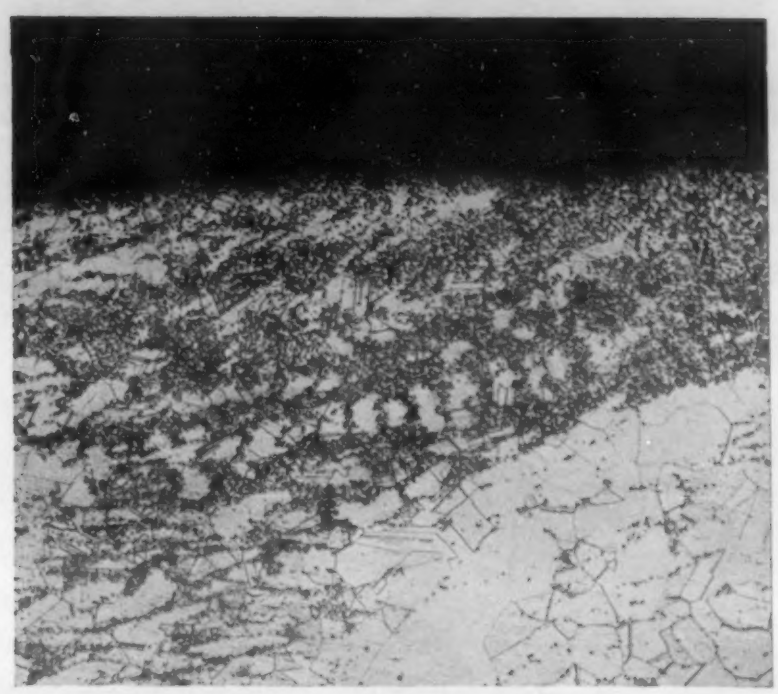
Table II.—Composition and Physical Properties of Cable Sheath Materials*

	Lead	Copper	Tin	Antimony		Tensile Strength, lbs. per sq. in.	Elongation in 2 in., per cent	10,000,000 Cycles Fat. Limit, lbs. per sq. in.
Common lead	99.85	....	....	....		1900	50	400
Copper bearing or Chemical.....	99.85	0.06	....	....		2300	40	600
2% tin alloy	98.00	....	2.0	....		3000	45	800
1% antimony alloy	99.00	0.06	....	0.85	Calcium	4200	10	1200
0.04% calcium alloy.....	99.85	0.06	....	....	0.035	4000	30	1400
					Tellurium	2800	45	900
0.07% tellurium alloy	99.85	....	....	....	0.07			
		Cadmium						
1 BNF	99.25	.25	....	0.50		4200	15	1200
2 BNF	98.25	.25	1.5	....		2800	30	900

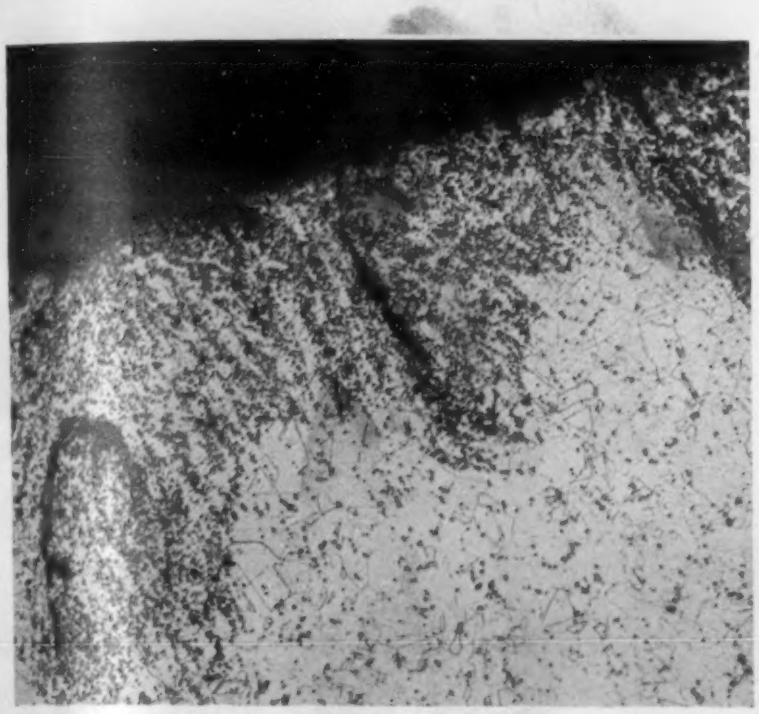
* Figures obtained from data published by various authors.



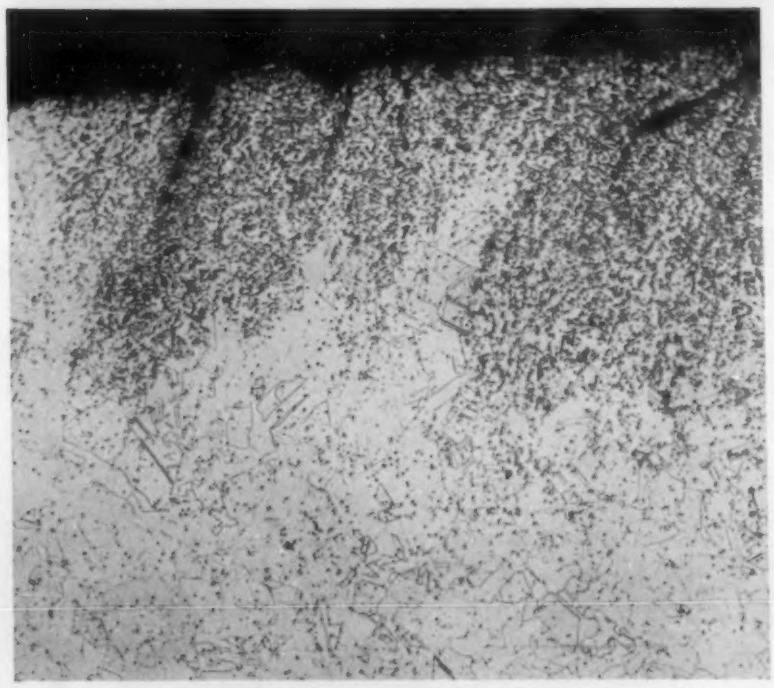
After 1st hot roll pass.



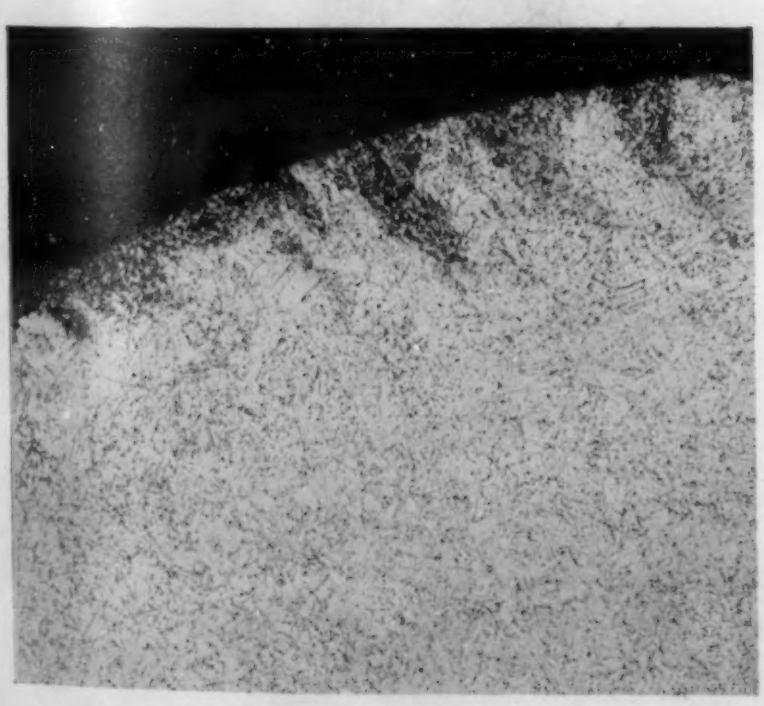
After 5th hot roll pass.



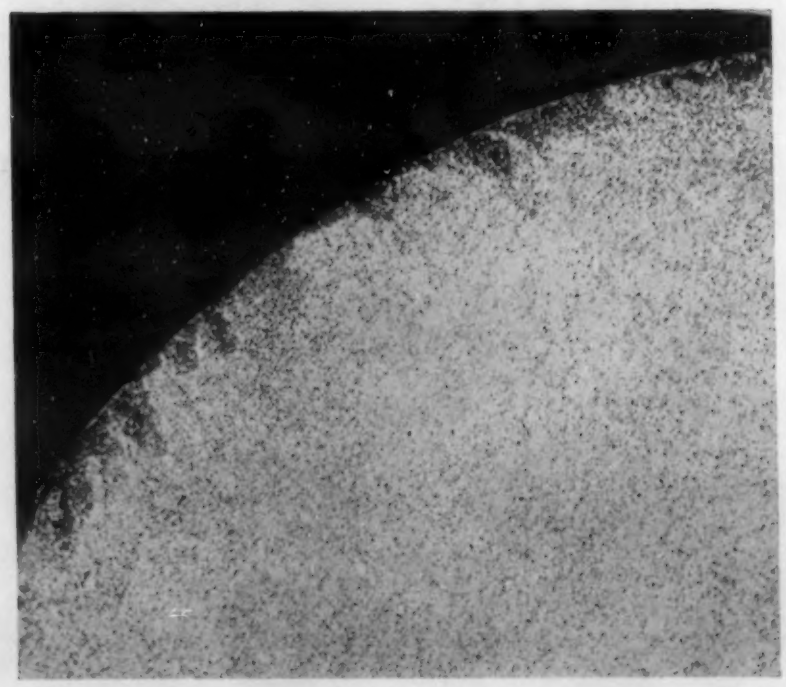
After final hot roll pass.



After 1st cold draw.

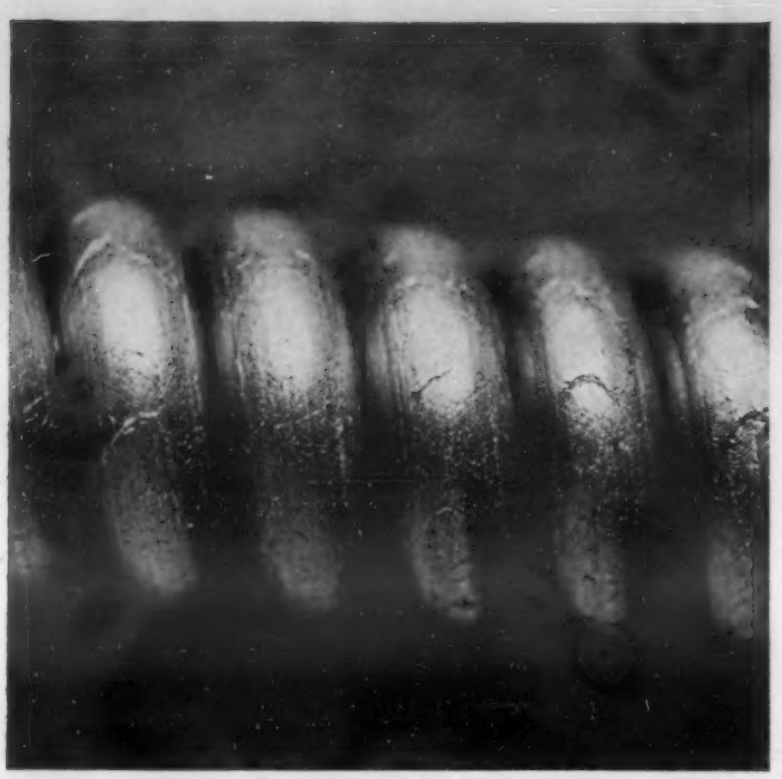


After 3rd cold draw.

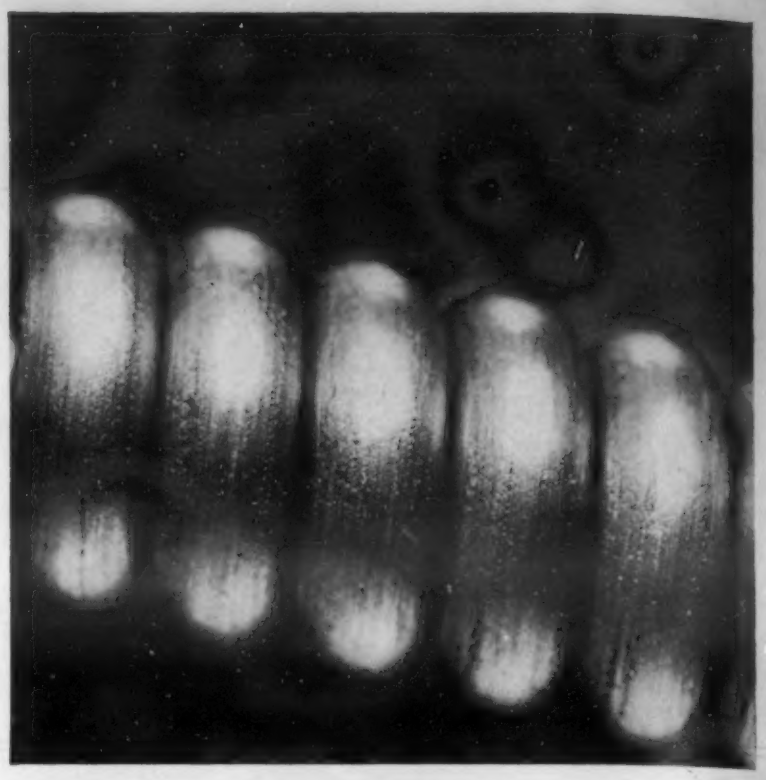


After final cold draw.

Details of Structure at Top Edge of Standard Electrolytic Copper Bars and Wires in Various Stages of Manufacture. Magnification of each one is 100 X.

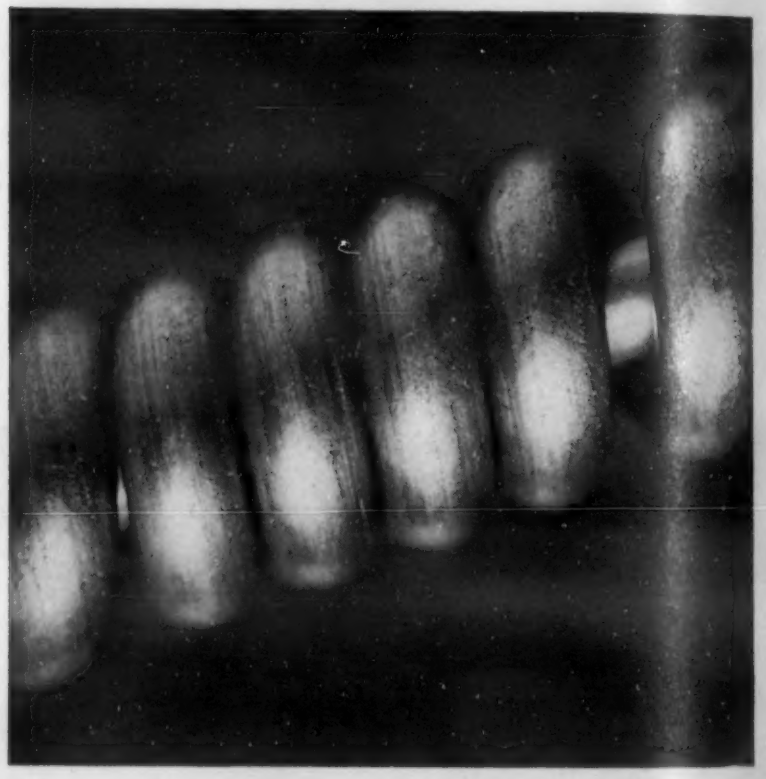


Surface checking of wire made from standard electrolytic copper.



Same wire as shown at left wrapped with opposite surface exposed.

Wire made from scalped electrolytic copper.



Wire made from end poured electrolytic copper.

Typical Appearance of Wrap Specimens of 0.104-In. Hard Wire Made from Various Types of Electrolytic Copper Wire Bars. Magnification 5 X.

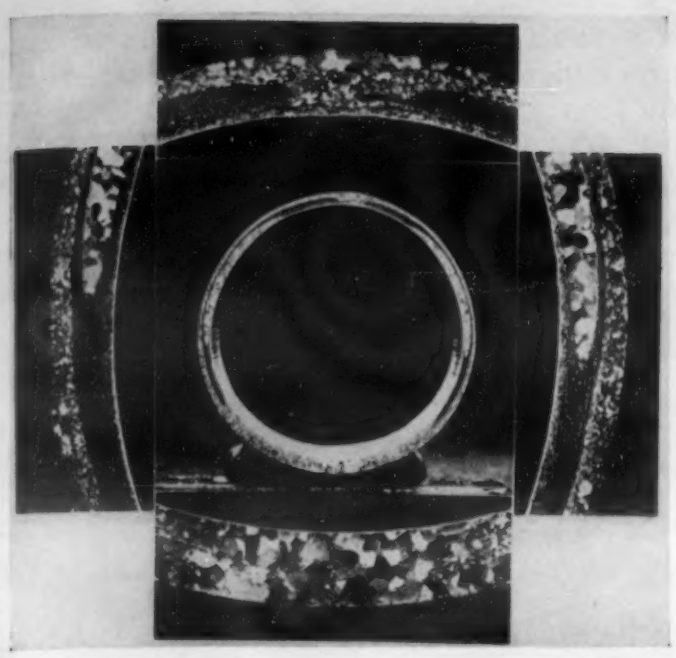
as lead pipe had been in commercial use for generations. The age of the art of the production of lead pipe is readily illustrated by the finding of lead water pipes in the ruins of the early Egyptian cities.

In 1844 Morse experimented with a four-conductor telegraph cable for use between Washington and Baltimore. The conductors were No. 16 gage copper wire, insulated with cotton saturated with shellac. The cable was drawn into a close fitting lead pipe and then the lead was drawn down onto the insulated conductors by passing the assembly through rollers.

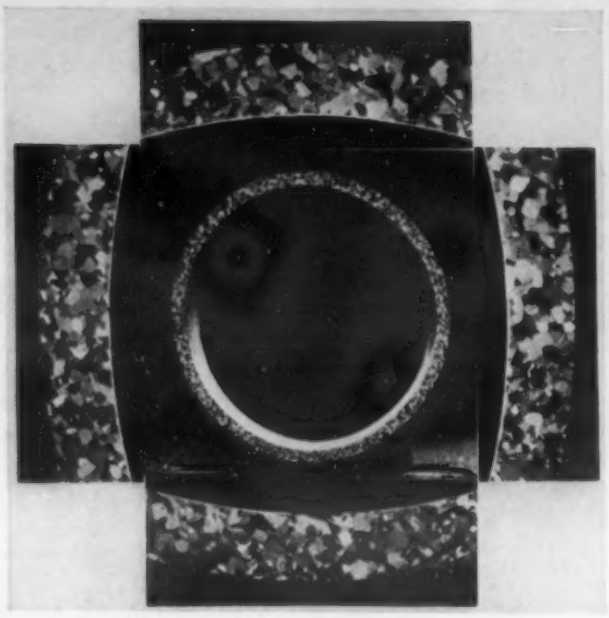
J. W. Marsh reported in the Waring Cable Handbook the extrusion of lead sheath over insulated power cables during the year 1883. About 1890 the Norwich Wire Co. manufactured the first power cable insulated with narrow paper strips, saturated in a rosin compound and covered with a lead sheath. During the past 50 years, the outer metallic covering of power cables has continued to consist mainly of commercial lead sheaths.

In the communication field 3 per cent tin-lead alloy sheaths were standard with the American Telephone & Telegraph Co. from 1894 to 1913. One per cent antimony-lead alloy sheaths were adopted by the American Telephone & Telegraph Co. in 1913 and have continued to be their standard for aerial service up to the present time.

Two per cent tin-lead alloy and 1 per cent tin-lead alloy sheaths have been used on power cables which were subjected to vibration. These alloys having a higher fatigue limit are used successfully in places where commercial lead sheaths are destroyed rapidly due to fatigue cracks. Fail-



Structure in Critical Region of Old Cable Sheath.



Uniform Structure in Critical Region of Modern Cable Sheath.

ures of this type have been practically eliminated by selecting the alloy which will have a fatigue limit greater than the stress to which the cable sheath is to be subjected.

In Great Britain ternary alloys have been used because of their higher strength and increased resistance to fatigue. These alloys contain cadmium and antimony, or cadmium and tin, alloyed with lead. Another British invention was the tellurium-lead alloy which has physical properties comparing favorably with the very high fatigue resistance of the calcium-lead alloy recently developed by the Western Electric Co. This material has been used in experimental installations by the American Telephone & Telegraph Co.

The composition and physical properties of some of the typical cable sheath materials are tabulated in Table II.

The lead sheaths for power cables were manufactured by the same methods of extrusion which were developed for the production of lead plumbing material. In 1930 various manufacturers started a scientific study of methods for the improvement of the quality of their lead cable sheaths. A systematic investigation of defects in cable sheaths was undertaken and methods developed for the preparation of lead and lead alloy cable sheath for microscopic examination.

It was found that irregularities in the structure of the lead could be eliminated by improved foundry practice. One of the first steps in improving the foundry conditions at the press was to recast the lead scrap into pigs and prevent oil soaked scrap, wood splinters, cement dust, etc., from being introduced into the lead melting kettle used in supplying the lead press. The second step in producing uniform sheath structures was improved pouring and skimming practices.

The band test was developed to determine the uniformity of the structure of the metal. The drawbench test was developed as a means for testing the quality of the welds in lead sheaths. The longitudinal or radial welds were eliminated by the Henley straight through press. Continuous presses which also eliminate the charge or circumferential welds are under development.

The IPCEA Technical Report No. 1, issued October, 1933, gives information regarding the various types of mechanical tests for laboratory use, as well as the methods used for microscopic examination of lead structures.

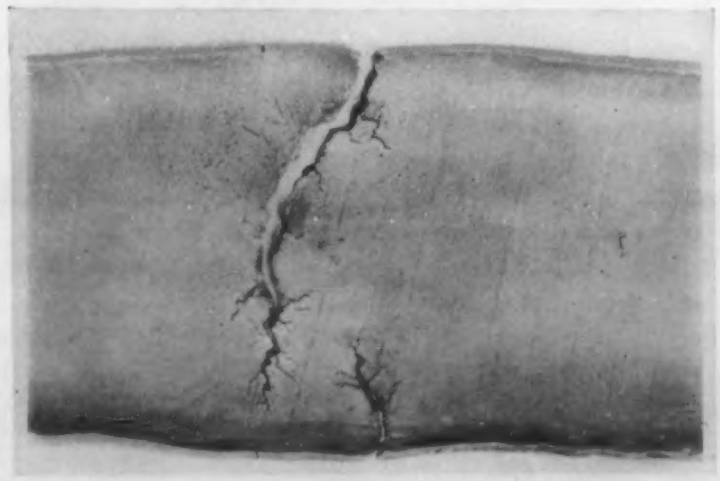
With the improved foundry practice it was discovered that the drawbench and bend tests would not always locate the minor defects and that it was necessary to first find the defect by means of microscopic examination and then stress the sheath at the point containing the defect in order to rupture the sheath in the questionable area.

This point is illustrated by Tables I and IV, and Plates 17 and 29 of the Joint AEIC-IPCEA Technical Report No. 2, issued September, 1936.

A fundamental change in handling the molten lead at the lead press was the use of a pipe in place of an open trough and the skimming or gating of the lead slug in the press. The additional steps which were added to the skimming and cropping method can be enumerated as follows:

1. Bottom pouring of the charge. In this method a seamless pipe is inserted to the bottom of the cylinder. After the molten lead has filled the cylinder, the pipe is withdrawn immediately after pouring.
2. Automatic mechanical cropping. This is accomplished either by a guillotine which is drawn across the top of the charge or by means of a truncated cone at the nose of the ram.
3. The use of carbon dioxide as a protective atmosphere to prevent the formation of oxide on the lead.
4. The electric arc method of melting the old charge before the new charge is added in order to float off the oxide from the old charge and effect the union of the two charges.
5. The burning hydrogen method to protect the molten lead against oxidation.

Lead Cable Sheath Failed by Vibration Fatigue.



6. The vacuum method to prevent the oxidation of the lead while being transferred from the melting kettle to the lead press.

If there is an excess of foreign material or dross present on the surface of the lead, the foreign material will not be eliminated by the burning hydrogen, vacuum, or any other of the special methods. The success of these processes, therefore, depends on supplying the lead press with clean material. As oxygen and lead oxide are not dissolved in lead, these materials can readily be separated from the lead. Therefore, by cropping the top of the lead in the cylinder, uniform structures can be obtained in the lead sheath.

In 1935 the A.S.T.M. pig lead specifications were revised to increase the lead content of the common lead pigs and comply with the needs of power cable manufacturers.

The work of Professor Moore at the University of Illinois has shown that the creep rates of various types of lead cross at a value between 300 and 400 lbs. per sq. in., when the lead is subjected to a continuous load at 65 deg. C. Common lead shows superior results at loads of 200 lbs. per sq. in., whereas calcium-lead shows superiority at loads of 400 lbs. per sq. in., when the temperature is maintained at 65 deg. C. Table III shows the days required to expand a lead sheath 1 per cent when subjected to various intermittent loads at 65 deg. C. Three of the samples described in the Joint AEIC-IPCEA Technical Report No. 2 are compared with tellurium-lead and calcium-lead alloy sheaths.

In the past few years there has been a decided improvement in the quality of the zinc coating of steel armor wires. Improved copper-rich alloy wires have also been developed which can be used when non-magnetic armor is required.

Table III.—Time for 2.73 in. O.D. Ring to Expand 1 Per Cent

	200 lbs. per sq. in.	250 lbs. per sq. in.	300 lbs. per sq. in.	400 lbs. per sq. in.	600 lbs. per sq. in.
Desilvered lead, 99.85% pure, IPCEA Sample No. 7	486 days	196 days	43 days	App. 5 days	.....
Copper bearing desilverized lead, 99.85% pure, IPCEA Sample No. 6	282 days	186 days	93 days	13.5 days	.....
ASTM Grade II lead, IPCEA Sample No. 9	261 days	189 days	123 days	43 days	App. 6 days
0.007% tellurium-lead	201 days	166 days	153 days	108 days	52 days
0.035% calcium-lead	258 days	219 days	186 days	138 days	84 days

Note: Intermittent loading—8 hrs. on, 16 hrs. off. Measured with load released.

A new type of cable sheath has been developed which consists of a laminated sheath made up of layers of copper tape which are bound together in a homogeneous mass by means of solder.

Improvements in the art of welding and the uniform quality of steel pipes have aided in the commercial development of pressure type cables. The development of silicon bronze alloy pipes and the technique of welding them has made it possible to use this non-magnetic material when corrosive conditions require the installation of other than ferrous material.

A review of the metals used in power cables indicates that the metal industry has succeeded in developing new materials as they were required to meet improvements in the art of power cables.

Editorial

(Continued from page A 21)

ness on single quench, too great depth hardening of the core, and distortion on double quench, though it was recognized that the case was wear-resistant, not liable to spalling, and that the rate of carburization was good.

The conclusions of these workers were quoted or summarized in books appearing in '25, '27, and '32 and culminated in the pronouncement in the '36 A.S.M. Handbook with the statement "The use of molybdenum steel containing chromium is not recommended, as this steel has an inherent tendency to distort in the carburizing operation." More expensive steels were resorted to.

The Germans were not awed by the conclusions of the American carburizing experts, and by '35 had included in their carburizing steels one with the same chromium, higher manganese, and slightly lower molybdenum, which they found useful, the main precaution being to hold the carburizing temperature down so as not to build up too high a carbon content in the case.

In the United States some inquiring soul set out to reexamine the situation, cut the chromium and molybdenum a bit, chose a fine-grained steel, normalized it before carburizing, and tried it on a single quench, all perfectly logical moves for increasing core toughness and avoiding distortion. The results showed that the previous faults were erased. Here, as in so many cases, appreciation of grain growth propensities made previous dogma untenable.

It isn't safe to believe all the books tell us, nor what the experts conclude, when such comments don't line up with underlying principles. The experimental facts reported are usually correct for the particular conditions, but the generalizations drawn from them may be much in error. Nor do repetitions make a half-truth into a whole truth.

It wouldn't be a bad idea to include a course in skepticism in the sophomore year of a metallurgical curriculum.—H. W. G.

A Suggestion

At one of the symposia recently presented at the convention of a large technical society, several of the authors presented data as tables in the form of slides. In most cases the data were indistinct and impossible to grasp. Nor was the printed information readily available or, if it was, it had been handed to listeners as they entered the room and could not be satisfactorily examined in the limited time nor in the darkness. A nearby metallurgist suggested that it would be much better, whenever possible, if such data were shown as curves instead of as figures. There is much point in this remark. A chart can be much more quickly analyzed than a table of figures. We believe the suggestion is worth the serious consideration of authors and program committees.—E. F. C.

TRENDS IN PRODUCTION OF

American Alloy Steels

AND OF ELECTRIC STEELS

by Edwin F. Cone

THIS ARTICLE IS AN ATTEMPT to clarify the situation as to the statistics of the country's production of alloy steel, of alloy steel castings and of total electric steel. Such a clarification seems necessary because the data of the American Iron and Steel Institute, excellent and reliable as they are, are incomplete. This is not due to any fault of the Institute.

As stated in an article in METALS AND ALLOYS for April —"Production Data of the Steel Foundry Industry"—the statistics of the American Iron and Steel Institute are complete, or nearly so, as to steel ingots, but as to castings they are decidedly incomplete. It was there stated that this is due to the establishing by the New Deal of Codes of Fair Practice in 1933. From 1934 to date the only production data for steel castings collected by the Institute are those for ingot producing companies which produce castings in their own foundries and these are not directly segregated. In the article just referred to, data for the steel foundry industry were published through the cooperation of the Steel Founders Society of America of Cleveland. With the further cooperation of that organization, it has been possible in this article to supplement the regular published data of the Steel Institute and to present at least a fairly reliable estimate of the country's alloy steel production and thus to show the trend.

Total Alloy Steel

In Table 1 are presented the data for the production of the alloy steel ingots and castings in the United States in gross tons. To and including 1933, the Institute's data are largely only ingots, because the founding of the codes set up agencies for collecting foundry data which still exist —as for example the S. F. S. A., the Alloy Casting Association for corrosion and heat resisting castings and the Manganese Steel Founders' Society.

Therefore, the data for 1934, 1935 and 1936, as published by the Institute, have in Table 1 been modified by estimated additions of actual alloy steel casting production. It is estimated, on the advice of the S. F. S. A. that in 1934, 1935 and 1936, the percentage of alloy steel castings of the total steel castings was approximately 13 to 15.8, 14 to 17.2 and 15 to 18.6 per cent respectively. On this basis the American steel casting production in gross tons (see METALS AND ALLOYS, April 1937, Table II, page 113) would be as follows:

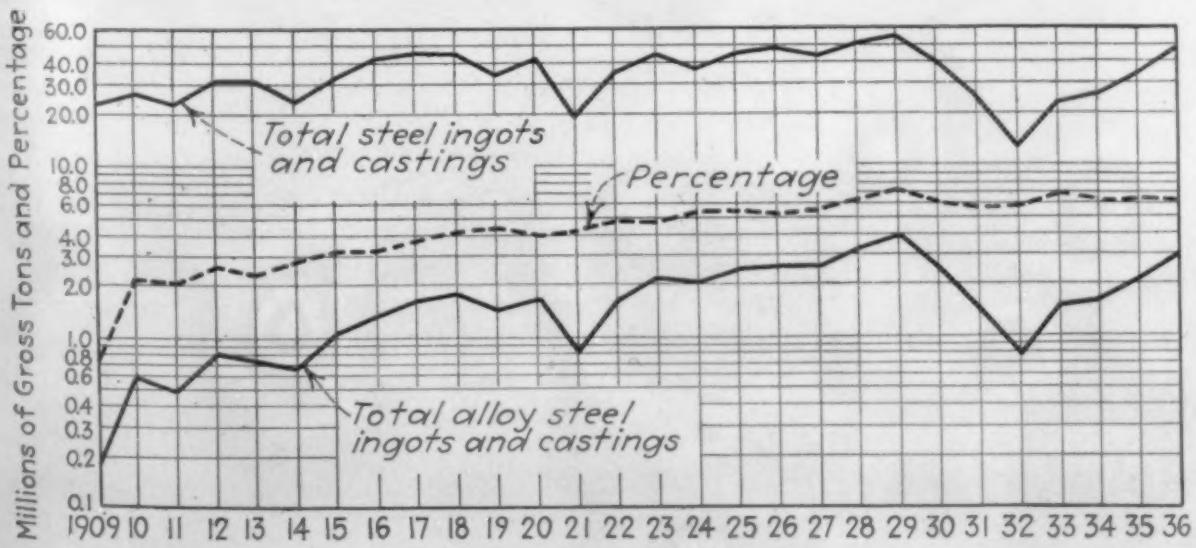
Table II.—American Steel Casting Production in Gross Tons[1]

	Castings	Alloy	Alloy Per Cent
1921	559,713	40,255	7.2
1926	1,357,558	146,101	10.7
1929	1,583,040	192,920	12.2
1930	1,104,215	126,128	11.5
1931	516,579	89,903	17.4
1932	216,760	41,044	18.8
1933	338,061	71,783	21.2
1934	425,000*	61,625	14.5
1935	417,600*	64,700	15.5
1936	812,500*	134,000	16.5

* Steel Founders' Data in Column 3 in Table I in gross tons.

[1] This table, supplemented as indicated, is from the article on Production Data of the American Steel Foundry Industry, in the April issue.

In a similar manner Column 2 of Table 1 must necessarily be modified for 1934 to 1936. This is accomplished by adding, to the total steel production of the Institute, the steel casting production of the foundries of the country



How the Proportion of Alloy Steel to the Total Output Has Fluctuated in 28 Yrs.

Checking the Temperature of a Heat of Electric Alloy Steel As It Flows from the Furnace into the Ladle. An optical pyrometer is used. (Courtesy: Ford Motor Co.)

steel casting output for the last three years, Table 3 is obtained:

Table 3.—Total Electric Steel Output

	Ingots	Castings	Total	Total Steel	Electric Per Cent
1936	704,213	235,600 [1]	939,800	48,442,000	1.94
1935	521,818	171,200 [2]	693,000	34,438,800	2.01
1934	349,095	136,000 [3]	485,000	26,417,600	1.83
1933	299,808	121,395	421,203	23,232,347	1.81
1929	532,392	419,039	951,431	56,433,473	1.68

[1] 29% of 812,500. [2] 41% of 417,600. [3] 32% of 425,000.

The data in Table 3 afford a satisfying and encouraging picture as to the progress and recovery of the electric steel industry. In 1936 and 1935 the total electric steel output advanced to 2 per cent of the total steel made,—a new high figure. In addition the 1936 total of over 939,800 gross tons was only a little under the record output in 951,431 tons in 1929. Also to be noted is the large increase in electric steel ingots in 1936—704,213 tons—a new high. This probably reflects the larger demand for stainless steels.

Summary

Recapitulating the data here discussed, some of it naturally estimated but probably reliably so, the following facts stand out:

The trend in American alloy steel production is steadily upward.

Total estimated alloy steel output in 1936 of about 3,017,600 gross tons was the third largest on record. It was 6.23 per cent of the total steel production or close to record percentages.

In electric alloy steel a new record was made in 1936 at 617,000 tons (estimated). The increase in the last two years has been decided. For 1934, 1935 and 1936, the percentage of electric steel of the total alloy steel has been about 20.5 per cent—a new high figure.

All indications point to still greater expansion in 1937 and coming years.

A Protest

Again the writer cannot let this opportunity pass to demur at least as to the basis on which alloy steel statistics are collected—namely, the definition of an alloy steel as laid down by the American Iron and Steel Institute. Undoubtedly some present-day steels are alloy steels, according to metallurgists, which are not recognized by the Institute. If a more liberal and more accurate definition were the basis for the collection of data, it is probable the official data would make even a better showing for alloy steel production. With the growing use of the low-alloy, high electric steels and the low-copper steels, some of which are not now recognized, the volume of alloy steels would be even larger.

(395,000 net tons or 362,340 gross tons in 1934 and so on) for each year.

Thus for example in 1936 there were produced 3,017,600 gross tons of alloy steel which was 6.23 per cent of the total steel production of ingots and castings of 48,442,030 tons. While 6.23 per cent of alloy steel of the total is not a high mark, it compares favorably with previous years and at least shows that the alloy steel industry virtually held its own through the depression.

The 1936 alloy steel production of 3,017,600 tons was the third largest, exceeded only in 1928 and 1929.

Of interest also is the last column of Table 1, which shows the tons of total steel to 1 ton of alloy steel. According to the revised estimated totals, there were 16.0 tons of steel made in 1936 for each ton of alloy steel which is slightly in excess of the record in 1934 and 1935. These records have only been surpassed in the abnormal years of 1929 and 1933. Only 27 years ago—in 1909—when the alloy steel industry was in its infancy,—131.6 tons of total steel was made to 1 ton of alloy steel.

Table 1.—Production of Alloy Steel Ingots and Castings in United States—Gross Tons.

	Total Alloy Steel	Total Steel	Per Cent Alloy Steel	Tons of Total Steel to 1 Ton of Alloy Steel
1909	181,980	23,955,021	0.75	131.6
1910	567,819	26,094,919	2.17	45.9
1911	481,459	23,676,106	2.03	49.1
1912	792,501	31,251,303	2.53	39.4
1913	714,357	31,300,874	2.28	43.8
1914	646,953	23,573,030	2.75	36.3
1915	1,021,147	32,151,036	3.17	31.4
1916	1,362,615	42,773,680	3.18	31.3
1917	1,644,335	45,060,607	3.65	27.4
1918	1,787,852	44,462,432	4.02	24.8
1919	1,481,188	34,671,232	4.27	23.4
1920	1,660,292	42,132,934	3.94	25.3
1921	809,548	19,783,797	4.10	24.3
1922	1,673,496	35,602,926	4.70	21.3
1923	2,106,489	44,943,696	4.70	21.3
1924	2,026,409	37,931,939	5.35	18.7
1925	2,432,973	45,393,524	5.36	18.6
1926	2,463,414	48,293,763	5.10	19.6
1927	2,531,748	44,935,185	5.59	17.7
1928	3,214,909	51,544,180	6.23	16.0
1929	3,957,207	56,433,473	7.01	14.2
1930	2,443,311	40,699,483	6.00	16.7
1931	1,455,913	25,945,501	5.61	17.8
1932	798,604	13,681,162	5.84	17.1
1933	1,547,183	23,232,347	6.65	15.0
*1934	*1,673,900*	*26,417,629*	*6.34*	*15.7*
*1935	*2,184,300*	*34,438,868*	*6.35*	*15.7*
*1936	*3,017,600*	*48,442,030*	*6.23*	*16.0*

Electric Alloy Steel

There is always keen interest in the electric steel industry, both as to the electric alloy steel produced and as to the total electric steel made.

In Table 2 an attempt is made to supplement the data of the American Iron and Steel Institute for 1934, 1935 and 1936 by adding the estimated amount of electric alloy steel castings made by foundries which do not report to the Institute. It is reliably calculated that about two-thirds of the alloy steel castings is produced in electric furnaces.

Thus, in 1936 there were produced 527,762 gross tons of electric steel ingots and castings as reported by the Institute. To this then must be added 66 per cent of the 134,000 tons of alloy steel castings (as described under alloy steels in the first part of this article) made in 1936 which brings the total electric alloy steel to 617,000 tons. Similarly for 1934 and 1935 the figures are 340,300 and 455,700 tons respectively.

From Table 2 it is interesting to note that the percentage of electric alloy steel of the total alloy steel produced reached the highest recorded figure during the last three years, 20.3, 20.8 and 20.4 per cent. This is due, in part at least, to the increased use of the high chromium and Cr-Ni steels, or stainless types.

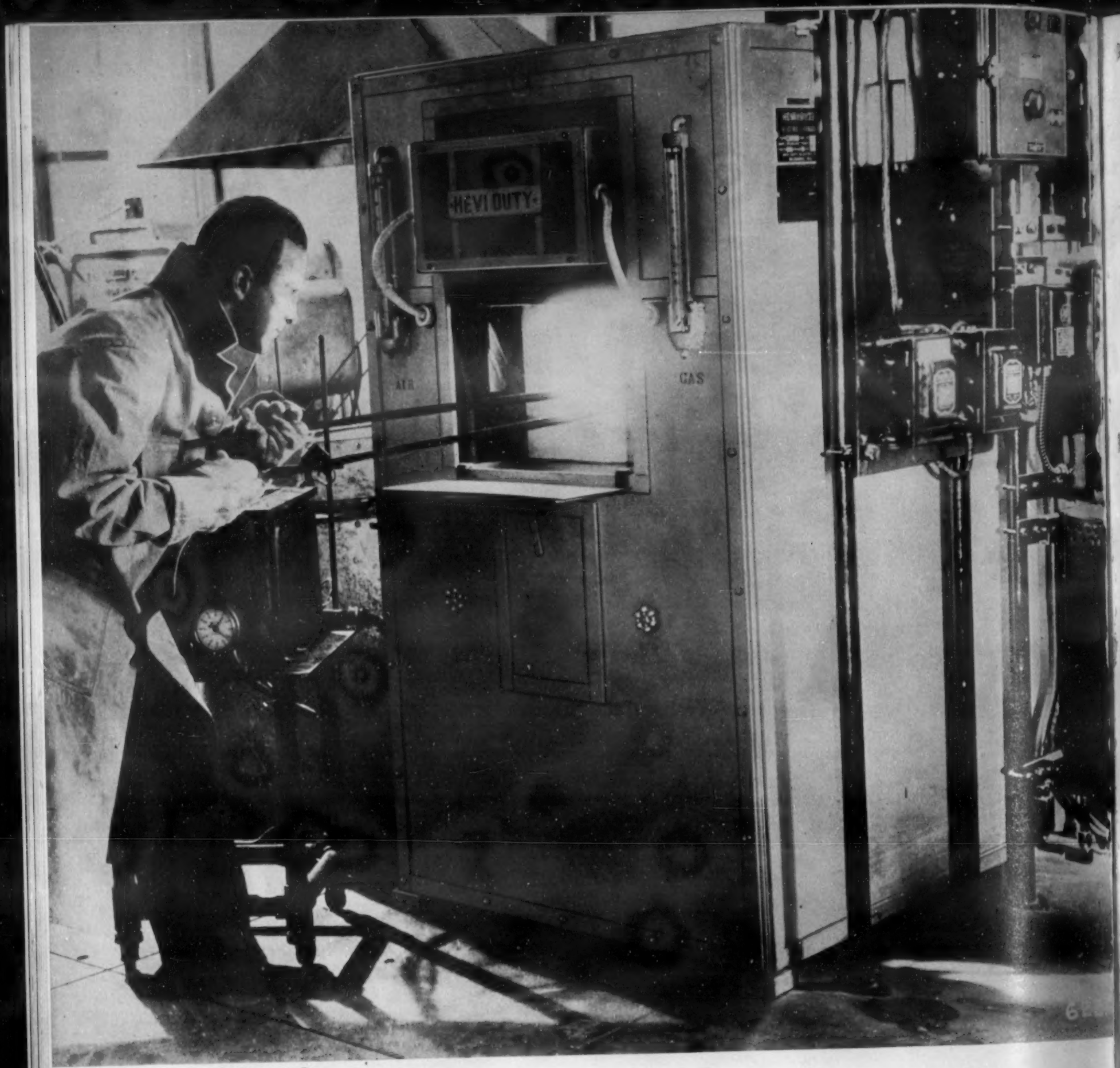
A Large Proportion of Alloy Steel is Made in Open-Hearth Furnaces. (Courtesy: Climax Molybdenum Co.)

Total Electric Steel

Substantial progress from the tonnage standpoint was made in 1936 in the electric steel industry. No actual data are published since 1933, as to the output of steel castings from electric furnaces. The S.F.S.A., however, estimates that in 1934 about 29 per cent of the total steel casting production was made in electric furnaces with 41 per cent in 1935 and 32 per cent in 1936. The American Iron and Steel Institute publishes the electric steel ingot production. Taking the latter and adding to it the estimated electric

Table 2.—Production of Alloy Steels made in Electric Furnaces in United States—Gross Tons.

	Electric	Total Alloy Steel	Per Cent of Electric Alloy Steel of Total Alloy
1909	.....	181,980	....
1910	608	567,819	0.11
1911	.....	481,459	....
1912	9,619	792,501	1.21
1913	11,264	714,357	1.57
1914	9,344	646,953	1.44
1915	27,944	1,021,147	2.73
1916	71,129	1,362,615	5.22
1917	130,578	1,644,335	7.94
1918	290,961	1,787,852	16.26
1919	181,632	1,481,188	12.26
1920	245,572	1,660,292	14.78
1921	63,246	809,548	7.81
1922	125,419	1,673,496	7.49
1923	194,976	2,106,489	9.25
1924	188,563	2,026,409	9.30
1925	293,780	2,432,973	12.00
1926	306,811	2,463,414	12.45
1927	343,517	2,531,748	13.57
1928	433,096	3,214,909	13.47
1929	510,030	3,957,207	12.87
1930	300,520	2,443,311	12.51
1931	232,113	1,455,913	15.94
1932	140,877	798,604	17.65
1933	296,210	1,547,183	19.11
*1934	*340,300*	*1,673,900*	*20.3*
*1935	*455,700*	*2,184,300*	*20.8*
*1936	*617,000*	*3,017,600*	*20.4*



urtesy: Hevi Duty Electric Furnace Co.

A Controlled Atmosphere Furnace for Heat Treating Steel.

AN EXPERIMENTAL STUDY OF

Gases for Controlled Atmospheres—II

IN THE HEAT TREATMENT OF STEEL

(Concluded from June Issue)

by E. E. Slowter and B. W. Gonser

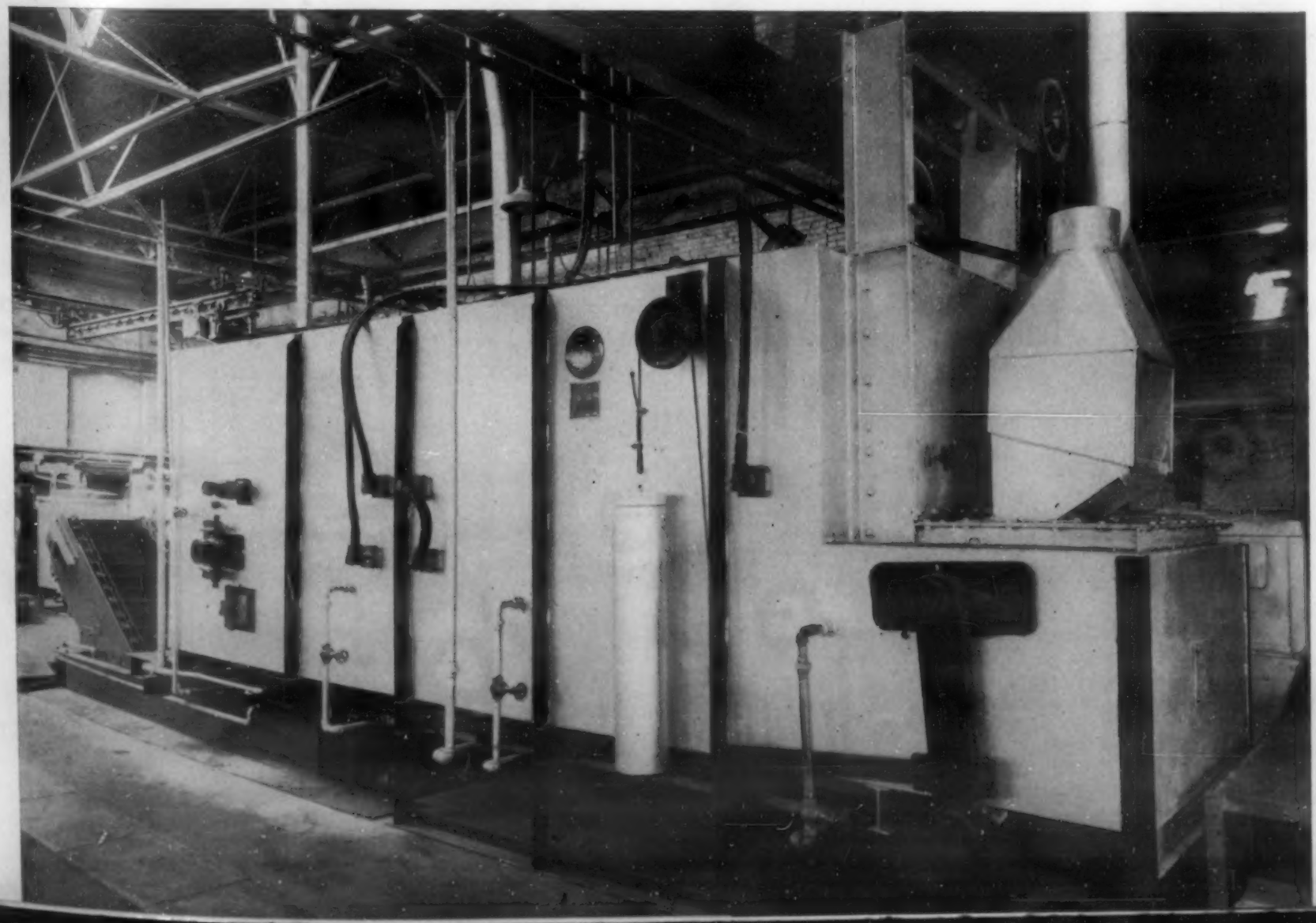
Chemical Engineer and Metallurgist, Respectively, Battelle Memorial Institute, Columbus, O.

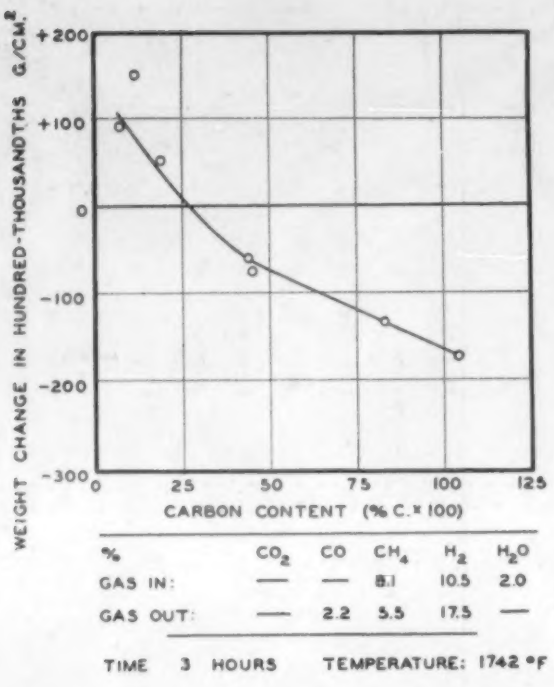
Carbon Monoxide-Nitrogen Mixtures

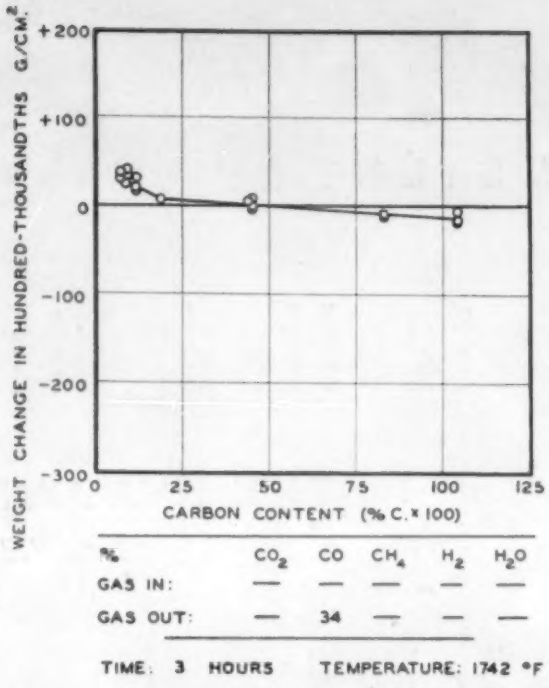
Turning now to CO-N_2 mixtures, note Fig. 19, 1740 deg. F. 3 hrs. Figs. 7 and 8 should also be consulted to show the effect of shorter times and lower temperatures. As CO is diluted down (even to pure N_2) with N_2, its mild carburizing action on low carbon and mild decarburizing action on high carbon steels, is reduced, as illustrated in Figs. 20, 21, 22, and 23. Five to 10 per cent CO has very little effect, and by addition of a trace of CH_4, as Fig. 24 shows, the very slight decarburizing action can be avoided.

Comparing Fig. 24 with Fig. 15, it can be seen that there is a lesser slope in the curve for CO made slightly carburizing with CH_4 than that for H_2 similarly treated. Thus a dry 5-10 per cent CO, 0.1-0.2 per cent CH_4, gas would avoid decarburization of carbon steels of *all* carbon contents and would produce but very slight carburization on the low carbon steels. It appears to be close to the ideal gas for bright hardening and bright normalizing in the range of steels, times and temperatures tested. This need not necessarily be true for alloy steels, especially those high

A Special Atmosphere, Continuous Chain Belt, Conveyor Type, Electric Furnace for Scale-Free Hardening Miscellaneous Small and Medium Sized Parts and Products Continuously. (Courtesy: The Electric Furnace Co., Salem, Ohio.)







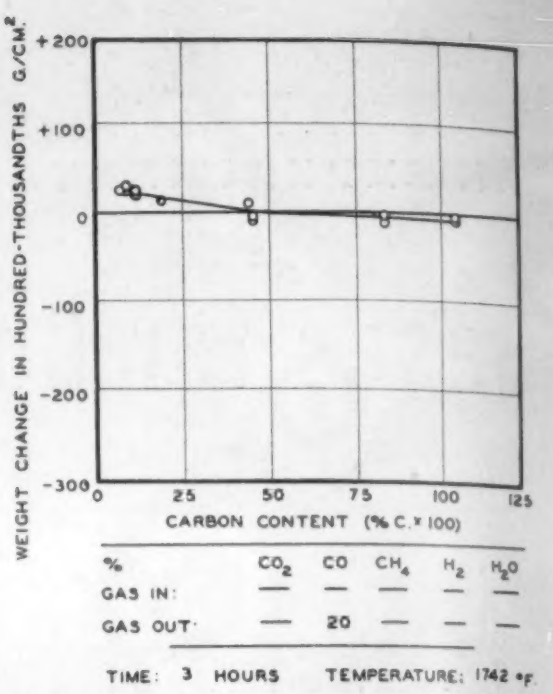
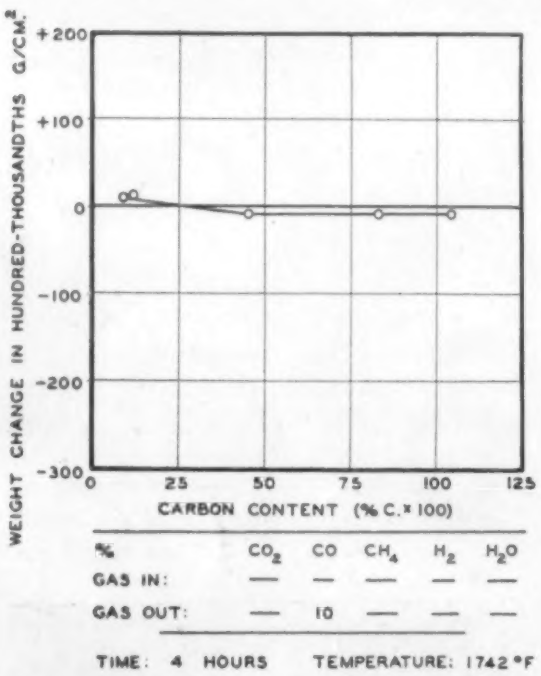
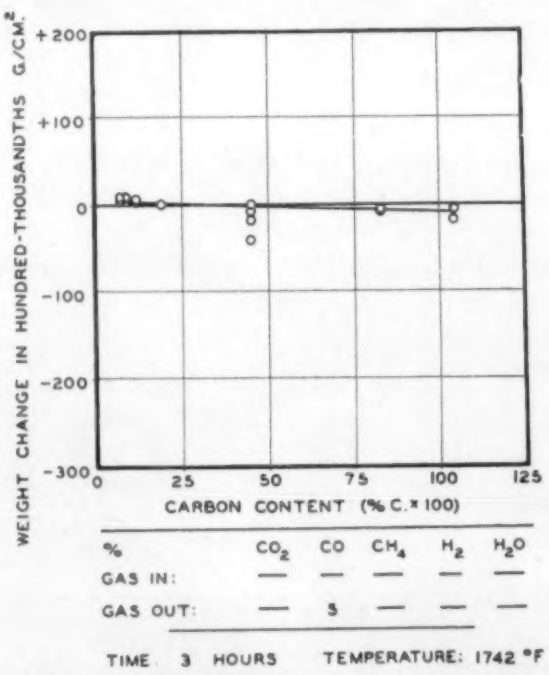


Fig. 18 (Left) Effect of Adding Natural Gas to a Moist Low Hydrogen-Nitrogen Atmosphere, High Carbon Steels at Gas Inlet. Specimens stained. Fig. 19 (Center) Action of 34 per cent Carbon Monoxide-Nitrogen Gas. This carbon monoxide content would be obtained by complete combustion to carbon monoxide of pure carbon in dry air. Fig. 20 (Right) Action of a 20 per cent Carbon Monoxide-Nitrogen Atmosphere.





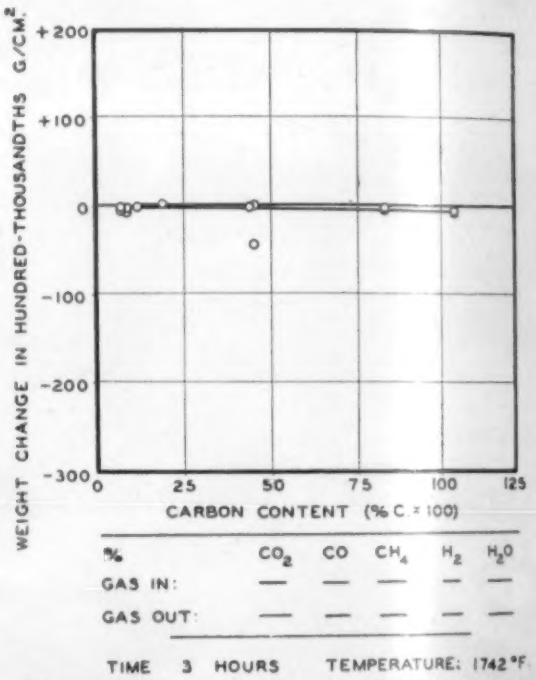
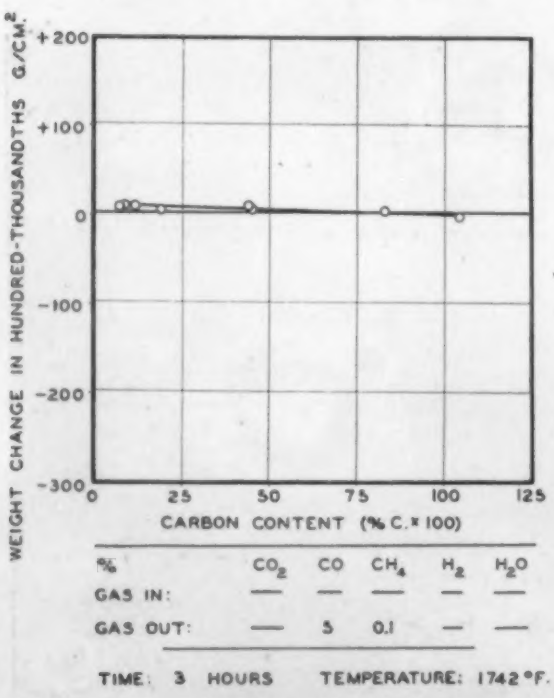
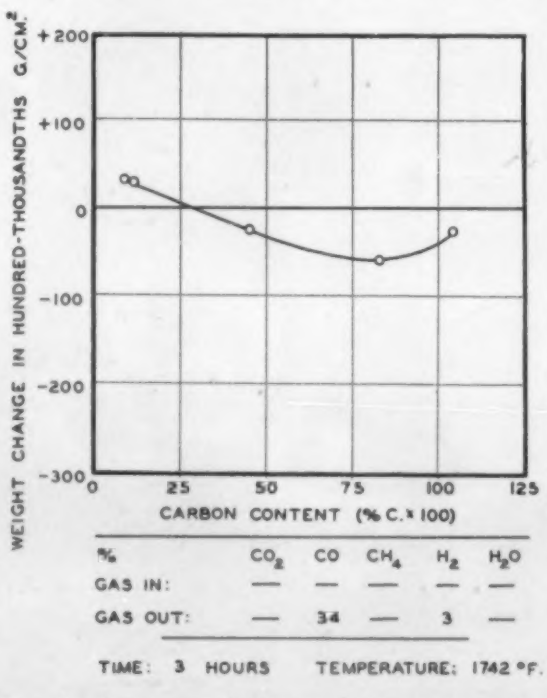


Fig. 21 (Left) Action of a 10 per cent Carbon Monoxide-Nitrogen Atmosphere. Fig. 22 (Center) Action of a 5 per cent Carbon Monoxide Atmosphere. Fig. 23 (Right) Action of Pure Nitrogen.





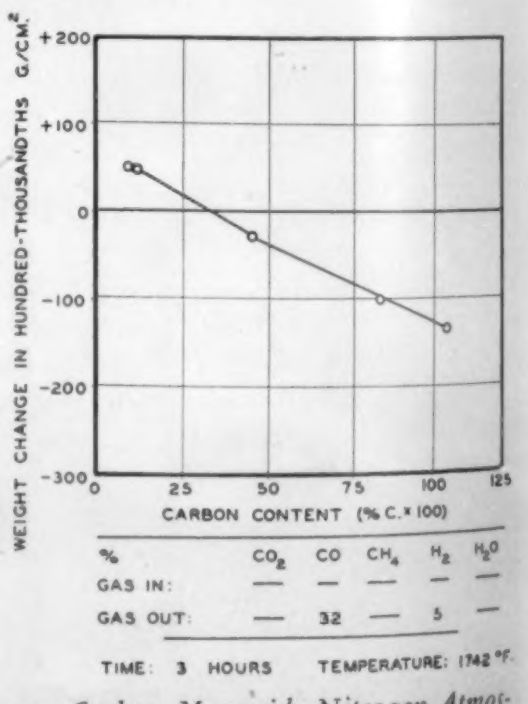
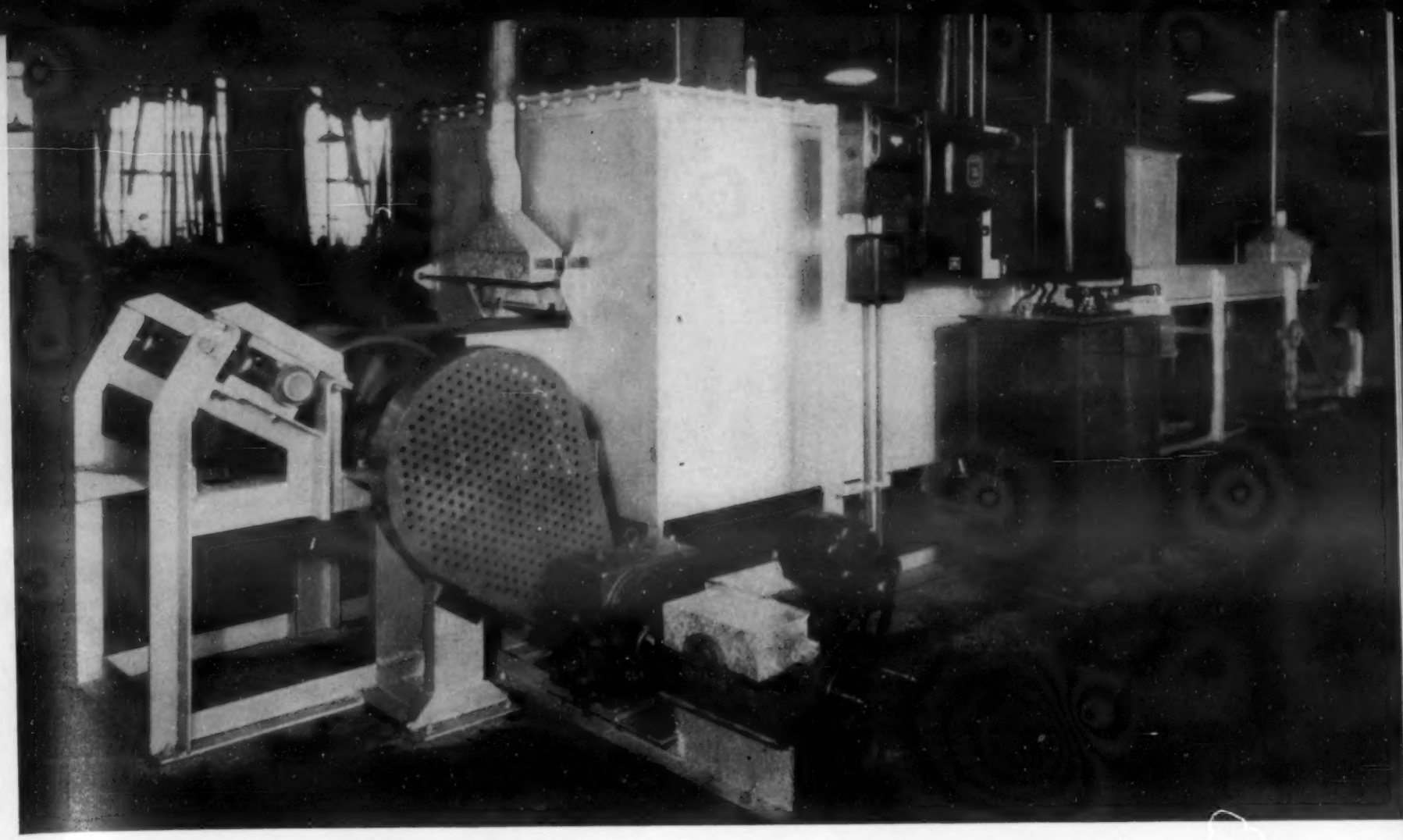


Fig. 24 (Left) Effect of Adding a Very Small Amount of Natural Gas to a 5 per cent Carbon Monoxide-Nitrogen Atmosphere. This gas fully accomplishes, for plain carbon steels, the result sought. Fig. 25 (Center) Effect of Adding Hydrogen to a High Carbon Monoxide Atmosphere. Fig. 26 (Right) Effect of Adding Hydrogen to a High Carbon Monoxide Atmosphere.



A 40 K.W. Electric Controlled Atmosphere, Brazing Furnace for Ferrous Parts. (Courtesy: Salem Engineering Co., Salem, Ohio.)

in Cr, since CO oxidizes such steels, and in such cases H_2 with an amount of CH_4 adjusted to the carbon content of the steel would be preferable.

If H_2 is also present with CO, the carburizing and decarburizing tendencies of CO are accentuated, as Figs. 25, 26, 27, and 28 show. This decarburizing tendency can be removed by CH_4 as in Fig. 29. While dry CO-H_2 mixtures are not so free from action as CO alone, they can be made neutral to any given carbon content of carbon steel. Such gases could be made from partly burned fuel gases by removing all CO_2 and H_2O. From the commercial point of view the production of dilute CO without H_2 is not simple. The high, 34 per cent CO, type of gas is more readily made.

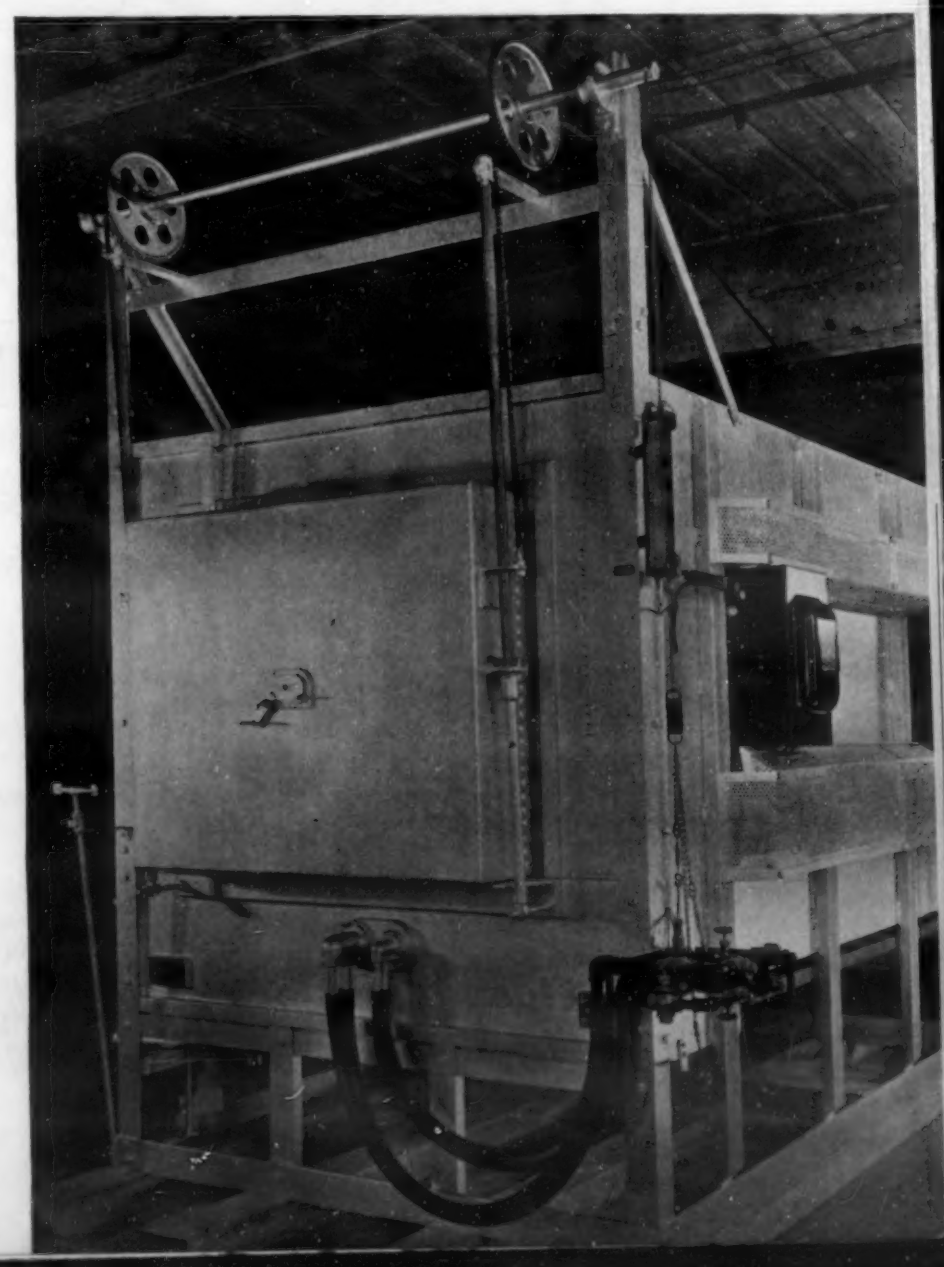
Like H_2, CO is adversely affected by H_2O. Fig. 30 shows the behavior of wet CO. Note the carburization and decarburization. That wet CO is an active gas is also shown by the change in composition of the gases. The specimens were dark gray to black but not stained as from oxygen. Assuming uniform water absorption by the inlet gas, there was no water in the outlet gas during the period at temperature. It was completely used up in the furnace.

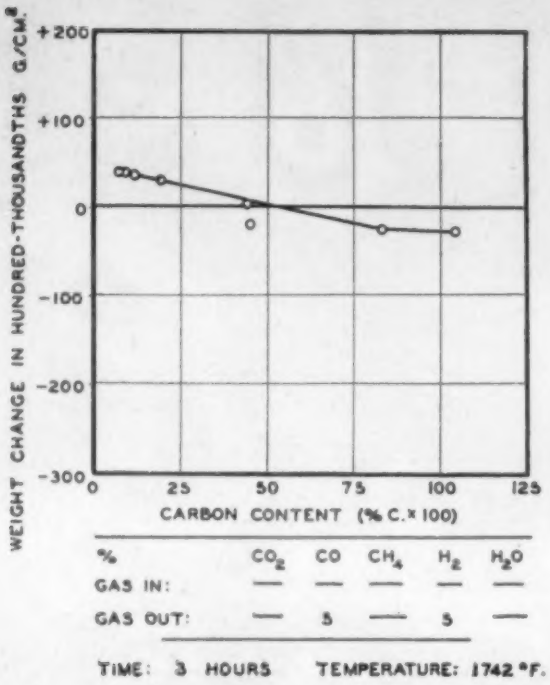
The question then again arises, can *moist* CO be adjusted by addition of CH_4? Comparison of Fig. 31 with Fig. 30 shows that the addition of 1.7 per cent CH_4 to the wet CO practically eliminated carburization of low carbon steels, although a carburizing gas was added, and vastly increased decarburization. The comparison of the gases in and out shows that the CH_4 reacted with the H_2O. The samples were dark gray.

Less H_2O and more CH_4 added to CO, as shown in Fig. 32, reduced the decarburization of high carbon steels and produced carburization of the low carbon steels. The gas changed as shown in the figures. The samples were blue-gray and were arranged with the high carbon steel at the gas inlet end.

If CO_2 is present in a CO-N_2 gas, the question arises, need CO_2 be removed, or can it be neutralized by addition of CH_4? Figs. 33 and 34 show that CO_2 has a strong decarburizing action. When the CO/CO_2 ratio is high as

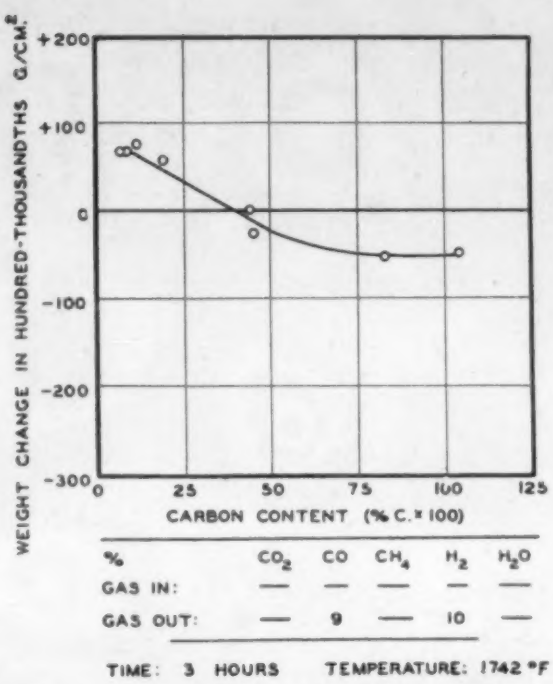
This Controlled Atmosphere "Certain Curtain" Furnace is Intended for Operation at Temperatures up to 2000 deg. F. for Heat Treating Large Dies of High Carbon Chrome Steel, etc. (Courtesy: C. I. Hayes, Inc., Providence, R. I.)





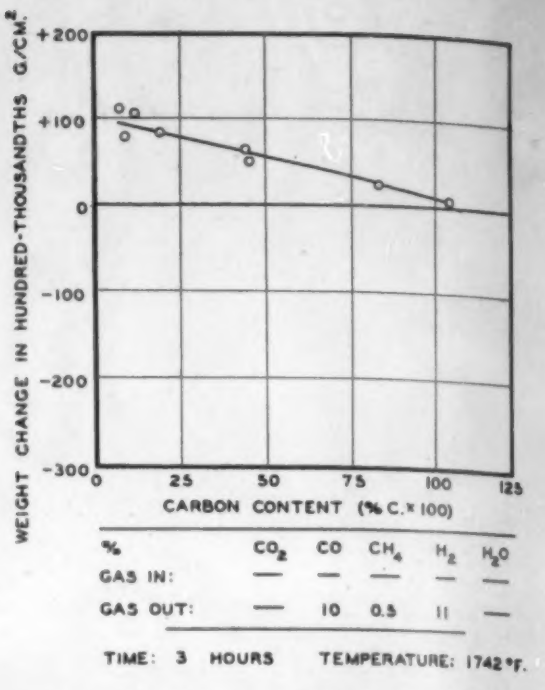
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	—	5	—	5	—

TIME: 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	—	9	—	10	—

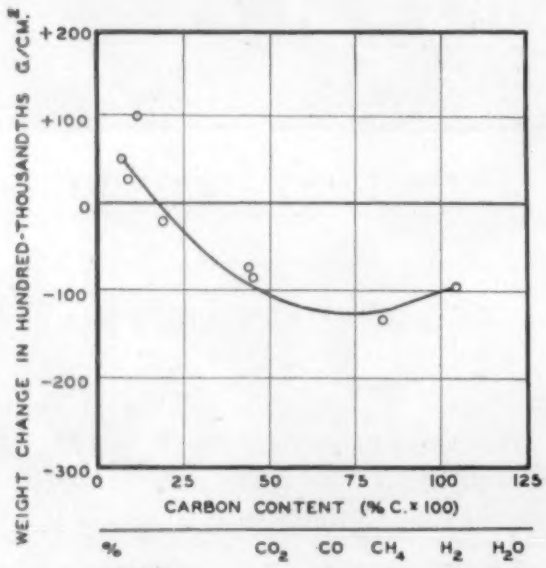
TIME: 3 HOURS TEMPERATURE: 1742 °F



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	—	10	0.5	11	—

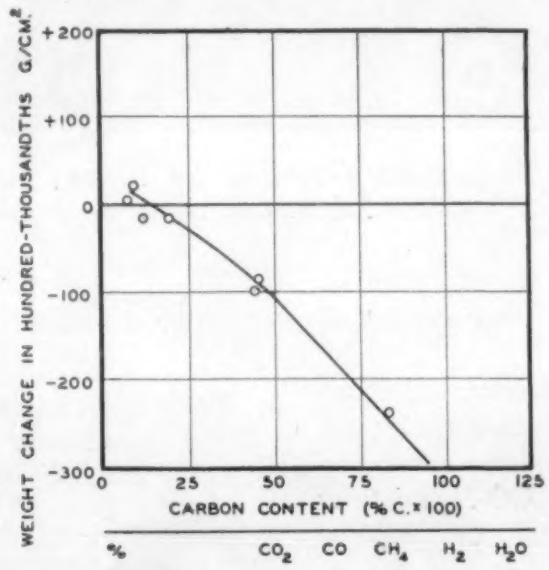
TIME: 3 HOURS TEMPERATURE: 1742 °F.

Fig. 27 (Left) Effect of Adding Hydrogen to a Low Carbon Monoxide Atmosphere. Fig. 28 (Center) Effect of Adding Hydrogen to a low Carbon Monoxide Atmosphere. Fig. 29 (Right) Elimination of the Decarburizing Action of a Hydrogen-Carbon Monixide Atmosphere by Addition of Natural Gas.



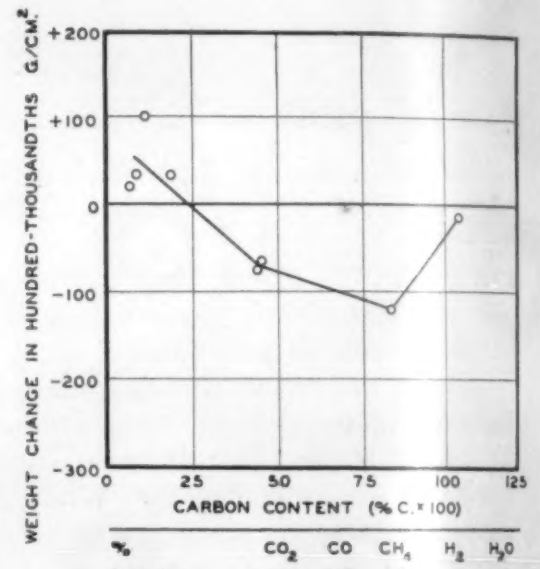
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	5	—	—	2.2
GAS OUT:	0.1	5.5	—	1.2	0

TIME: 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	5	1.7	—	2
GAS OUT:	0.3	5.6	0.9	1.8	0.4

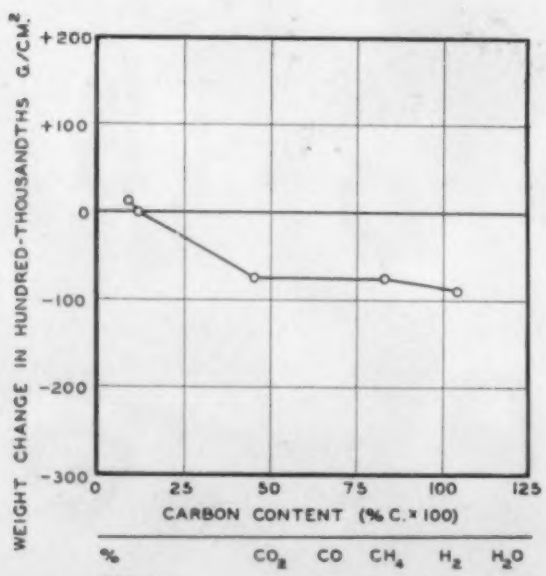
TIME 3 HOURS TEMPERATURE: 1742°F



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	4.8	4.5	—	1.4
GAS OUT:	—	8.1	2.9	4.2	0.1

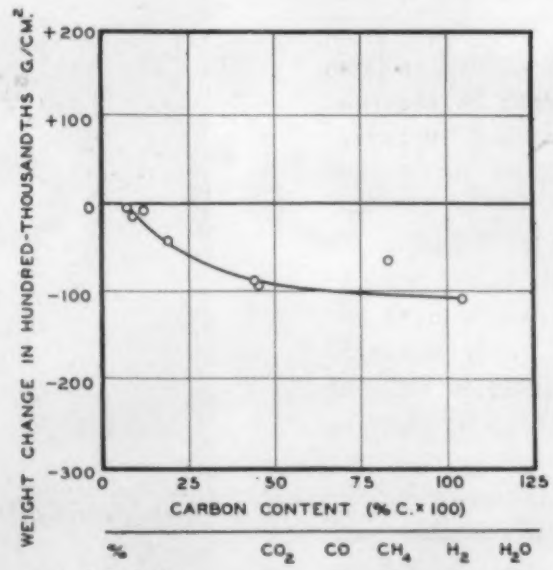
TIME 3 HOURS TEMPERATURE: 1742°F

Fig. 30 (Left) Action of Moisture with a Low Carbon Monoxide Atmosphere. Specimens darkened. Fig. 31 (Center) Failure of a Slight Amount of Natural Gas to Overcome the Decarburizing Action of a Moist Low Carbon Monoxide Atmosphere. Point for 1.04 per cent C is below the scale. Samples darkened. Fig. 32 (Right) Effect of Adding Natural Gas to a Moist Low Carbon Monoxide Atmosphere. Samples Darkened.



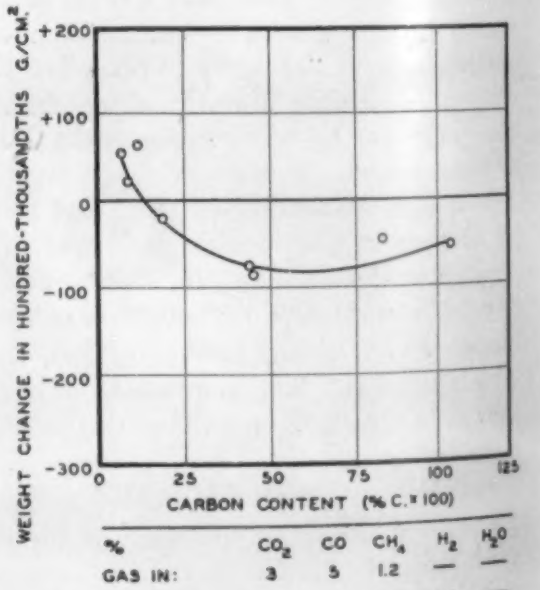
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	3	31	—	—	—

TIME: 3 HOURS TEMPERATURE: 1742°F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	3	5.5	—	—	—

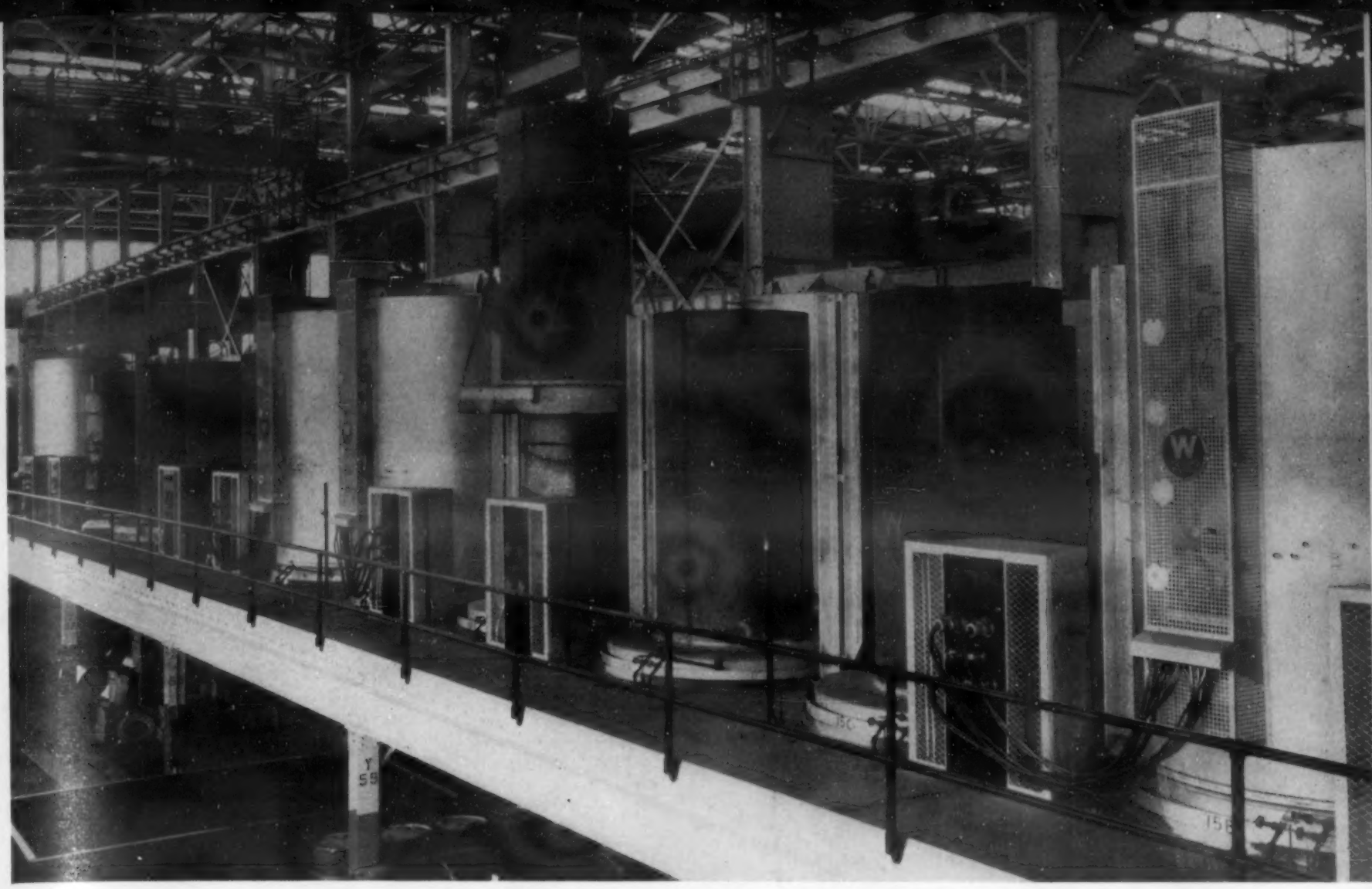
TIME: 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	3	5	1.2	—	—
GAS OUT:	2	7	0.7	1.3	—

TIME: 3 HOURS TEMPERATURE: 1742 °F.

Fig. 33 (Left) Effect of a High CO/CO_2 ratio on Decarburization. Samples clean. Fig. 34 (Center) Effect of a low CO/CO_2 ratio on Decarburization. Samples stained. Fig. 35 (Right) Effect of Adding a Slight Amount of Natural Gas to a Low Carbon Monoxide-Carbon Dioxide Atmosphere. Samples stained.



A Battery of Cylindrical Bell Type Furnaces for Bright Annealing Steel Strip in Coil Form. (Courtesy: Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.

in Fig. 33 the samples are fairly bright, but when low as in Fig. 34 the samples were all coated with a blue gray coat or scale.

When increasing amounts of CH_4 were added to this low $CO:CO_2$ gas, as in Figs. 35, 36, and 37, decarburization could be avoided but scale films were never completely avoided, and with the higher CH_4 contents there was a great tendency to precipitate carbon. The up-turn of the curves is probably due to the reaction of the gases in flowing through the furnace and the consequent diminution of the decarburizing effects. The effort to adjust this decarburization by CH_4 produces reaction between CH_4 and CO_2 as shown by the changing gas compositions in Table IV. The specimens were stained and soot was deposited.

Table IV.—Gas Reactions

		CO	CO_2	CH_4	H_2
Fig. 35	In	5	3	1.2	..
	Out	7	2	0.7	1.3
Fig. 36	In	5	3.4	2.9	..
	Out	8.4	1.3	1.5	2.5
Fig. 37	In	5.3	3	4.5	..
	Out	9.0	1.1	2.6	4.0

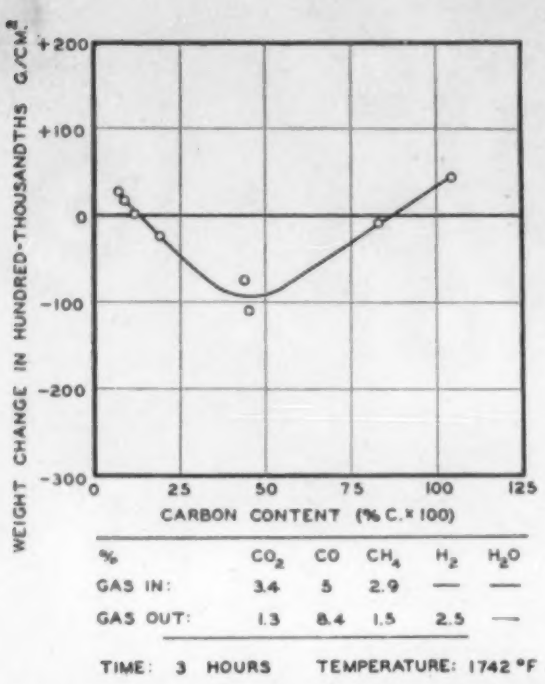
Synthetic Commercial Gases

We may now consider gases of the type made by partial combustion of fuel gases, with H_2O removed, but with CO_2 left. These will consist of CO, CO_2, H_2, and small amounts of CH_4.

Fig. 38 shows that these dry CH_4-free gases are decarburizing, but only mildly so to very low carbon steels. Remembering that Fig. 38 shows the exaggerated results of long time and high temperature, it is seen that these gases will serve for bright annealing of low carbon steels, but not for bright hardening of high carbon steels. As Figs. 39, 40, and 41 show, the trouble can not be avoided by raising the CH_4 if the CO_2 is kept around 5 per cent in the exit gas. Slight staining was encountered in these runs. If, however, the CO_2 is held low in the entrance gas, and the CH_4, CO, and H_2 contents are relatively high, this decarburization of high carbon steels can be reduced very materially, though at the expense of severe carburization of low carbon steels. This will be pointed out in later graphs on other synthetic commercial gases.

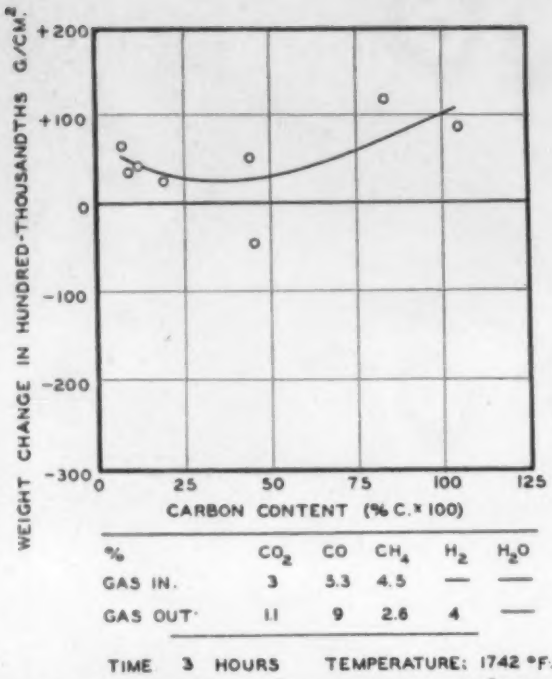
Produced Atmospheres

Attempted purification that does not remove all the CO_2 still leaves an active gas. This indicates that the gas should be purged of all its reactive components by allowing it to react with iron or steel before reaching the work, or treated in some other manner which will remove the reactive components. Now, as the gas analyses on Figs. 33 to 42 show, CO_2 in a gas mixture containing H_2 or CH_4, leads to a reactive gas, decarburizing to high carbon steels. By passing the partly burnt gas over iron in order to induce the reactions that would otherwise take place in contact with the work, and then leading it to the work, therefore, the evil effect of a reactive gas would be minimized. Such a treated gas should be decarburizing only from the accelerating effect of H_2O (produced by interaction of any CO_2 not removed, with H_2 or CH_4) on the action of the H_2 present. With drying, the behavior of the purified gas should approach that of a 9 CO, 10H_2 gas, (Fig. 28). An approach to this is shown in Fig. 42 where the samples were lightly oxidized. Fig. 43 represents a similar run, in which the dried combusted gases were passed over hot iron but without drying thereafter. The samples were bright but highly decarburized from the residual CO_2 and probably from H_2O formed by the reaction between CO_2 and CH_4.



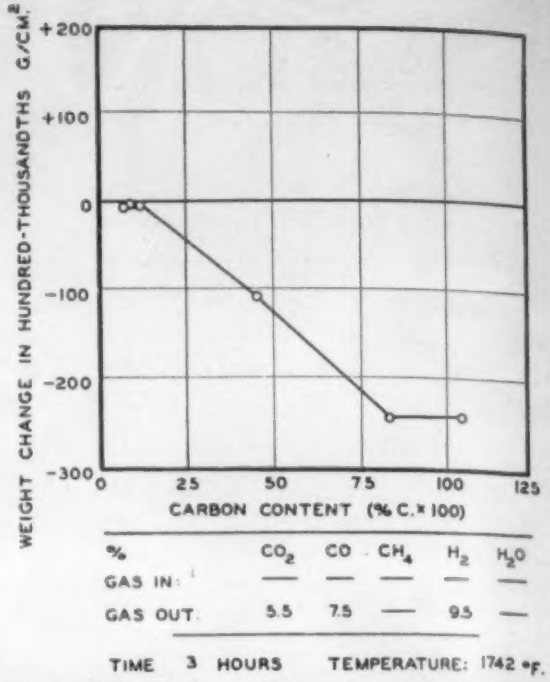
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	3.4	5	2.9	—	—
GAS OUT:	1.3	8.4	1.5	2.5	—

TIME 3 HOURS TEMPERATURE: 1742 °F



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN.	3	5.3	4.5	—	—
GAS OUT	11	9	2.6	4	—

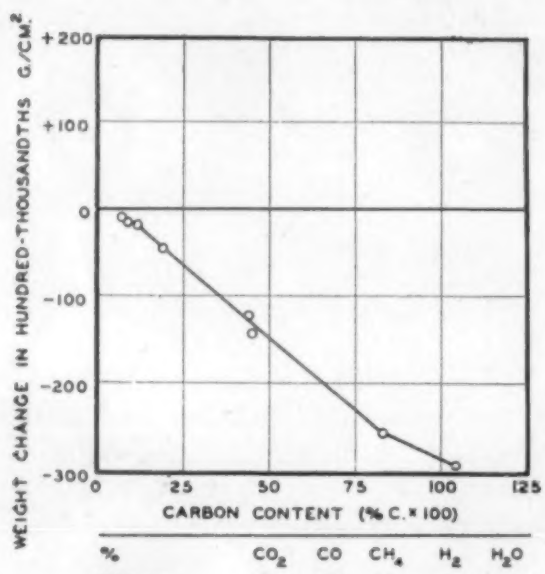
TIME 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT.	5.5	7.5	—	9.5	—

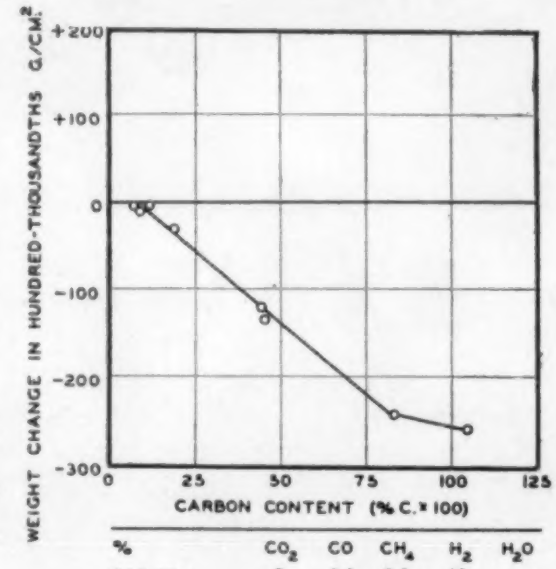
TIME 3 HOURS TEMPERATURE: 1742 °F.

Fig. 36 (Left) Effect of Adding an Amount of Natural Gas to a Low Carbon Monoxide-Carbon Dioxide Atmosphere. Samples stained. Fig. 37 (Center) Effect of Adding a Larger Amount of Natural Gas to a Low Carbon Monoxide-Carbon Dioxide Atmosphere. Samples stained. Fig. 38 (Right) Decarburization of Medium and High Carbon Steels by a Dry, Methane Free, Synthetic Commercial Atmosphere. Slight tarnish only.



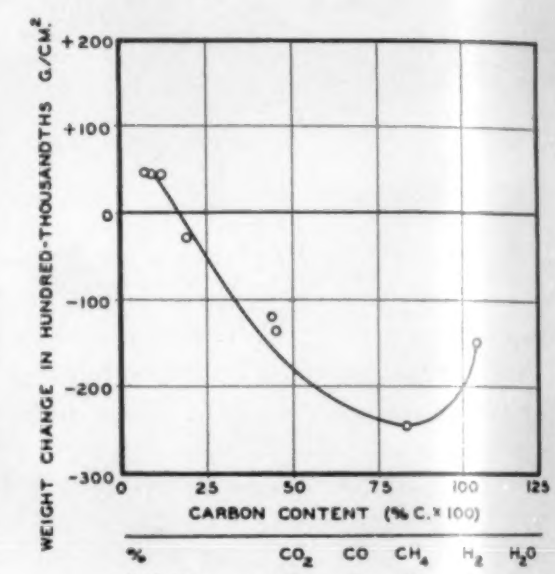
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN.	8	3.8	1.1	10	—
GAS OUT:	5	8	0.8	8.5	—

TIME 3 HOURS TEMPERATURE: 1742 °F



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	8	3.5	2.5	10	—
GAS OUT	5	8.5	1.5	11	—

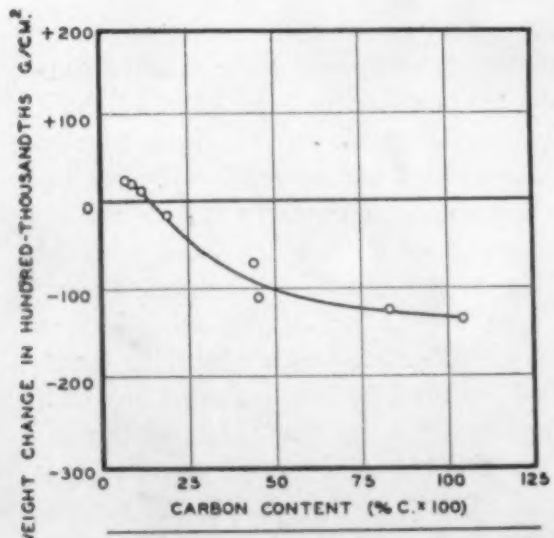
TIME 3 HOURS TEMPERATURE: 1742 °F



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	12	0	8	5	—
GAS OUT:	5	11	5	12	—

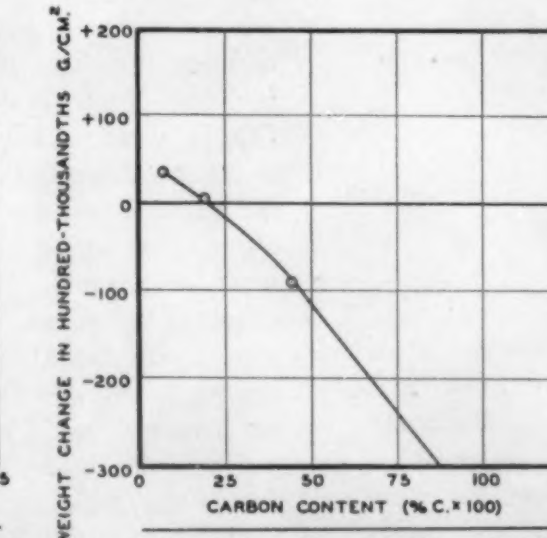
TIME 3 HOURS TEMPERATURE: 1742 °F

Fig. 39 (Left) Effect of Adding a Slight Amount of Natural Gas to a Dry Synthetic Commercial Atmosphere. Samples slightly stained. Fig 40 (Center) Effect of Adding an Amount of Natural Gas to a Dry Synthetic Commercial Atmosphere. Samples slightly stained. Fig. 41 (Right) Effect of Adding a Larger Amount of Natural Gas to a Dry Synthetic Non-Commercial Reactive Atmosphere. Samples slightly stained.



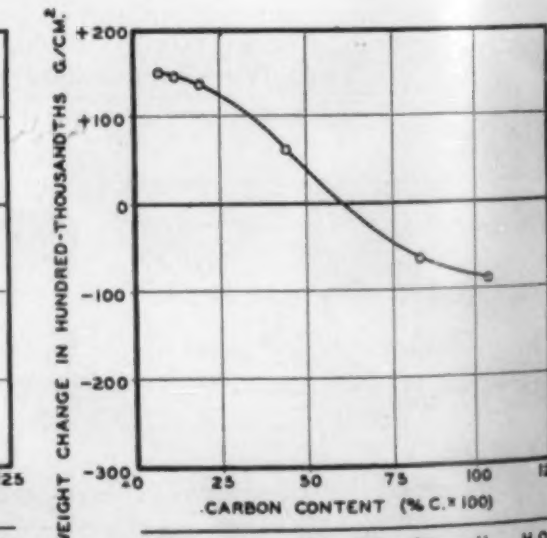
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN	—	—	—	—	—
GAS OUT:	0.1	11.5	0.8	13.8	—

TIME 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN.	—	—	—	—	—
GAS OUT:	0.8	15	0.4	35	—

TIME 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	—	14.5	0.5	28.5	—

TIME: 3 HOURS TEMPERATURE: 1742 °F

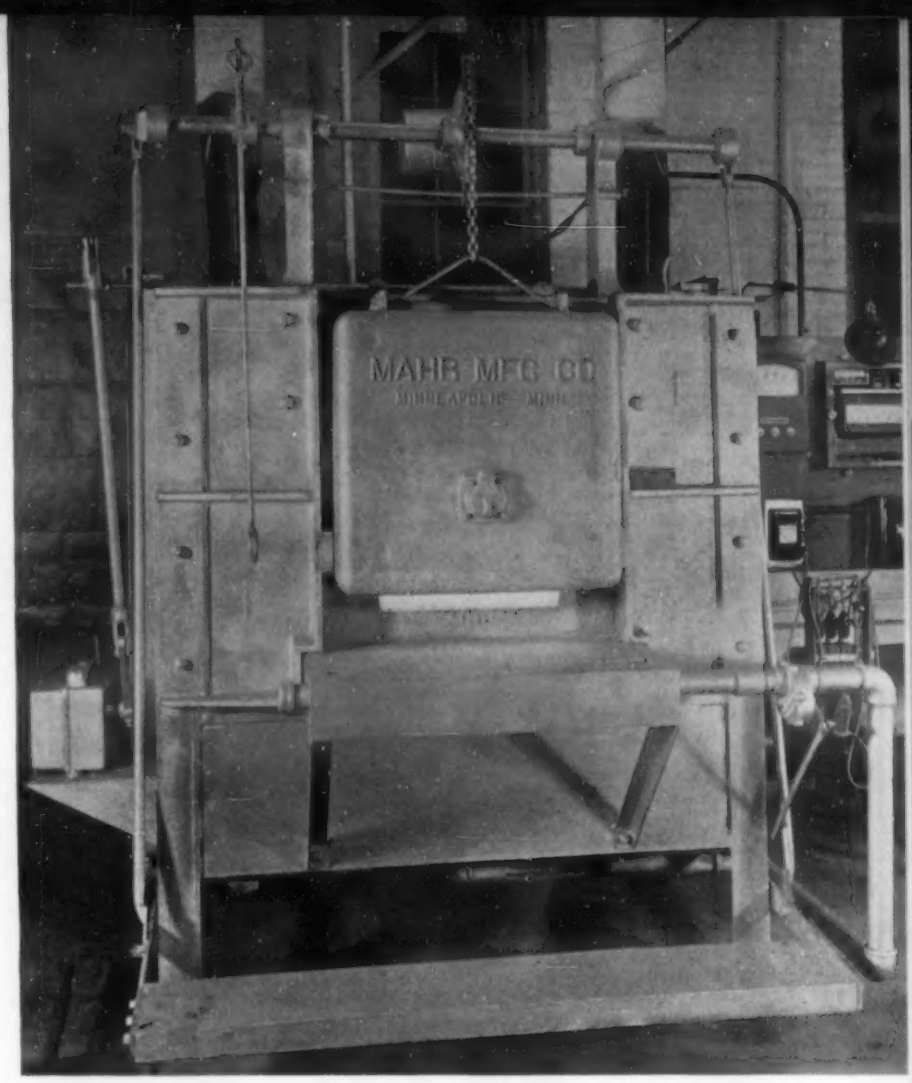
Fig. 42 (Left) Action of a Partly Burned Natural Gas Which Had Been Passed Over Hot Electrolytic Iron to Effect Reduction of Carbon Dioxide, Then Dried. Samples very slightly stained. Fig. 43 (Center) Action of a Partly Burned Natural Gas Which Had Been Passed Over Hot Electrolytic Iron; Dried Before but Not After Iron Treatment. Samples bright. High carbon samples badly decarburized. Fig. 44 (Right) Action of a Partly Burned Natural Gas Which Had Been Dried and Passed Over Soda Lime for Carbon Dioxide Removal. Samples bright.

Referring back to Fig. 29, however, it is seen that if *all* CO_2 and *all* H_2O are removed from partly burnt fuel gases, leaving only CO and H_2 with small amounts of unburnt CH_4, a further addition of CH_4 (or other hydrocarbon, e.g., bubbling the gas through benzol, C_6H_6) can be made to neutralize the decarburizing tendency. However different carburizing additions will have to be made to accommodate steels of different carbon contents. For instance, Fig. 44 shows results obtained with a dried, partly burned gas when the CO_2 was removed by soda-lime. The samples were bright and the gas did not react within itself. Fig. 45 shows a similar gas in which the CO_2 was eliminated by passage of the gas over hot carbon. Similar results were obtained. Such purified gases carrying CO as well as H_2 are in much the same position as straight H_2:N_2 mixtures; the CO is relatively neutral. Choice between H_2:N_2 and CO:H_2:N_2 will depend on the cost and certainty of purification of the latter gas made from the partly burnt fuel gases.

If preferential oxidation of H_2 could be accomplished by some catalyst to effect its complete removal yet leave some unburned CO, the resultant gas, freed from H_2O and CO_2, would be preferable to the CO:H_2 combination. Unfortunately, known catalysts work the other way as they favor burning of more CO and less H_2.

Of all the gases studied, the most universally useful atmosphere appears to be a 5 to 10 per cent CO, balance N_2 gas, free from O_2, CO_2 or H_2O, but perhaps with slight addition of CH_4, if such a gas can be made cheaply enough to be practical. If absolutely oxygen-free N_2 could be made cheaply enough, and if in its use, all infiltered air could be kept out, it would, of course, be a very satisfactory protective gas (c.f. Fig. 23) applicable to all carbon and alloy steels. The cost of cylinder N_2 and the necessity for having a little combustible gas to take care of traces of infiltered air, lead away from such a choice.

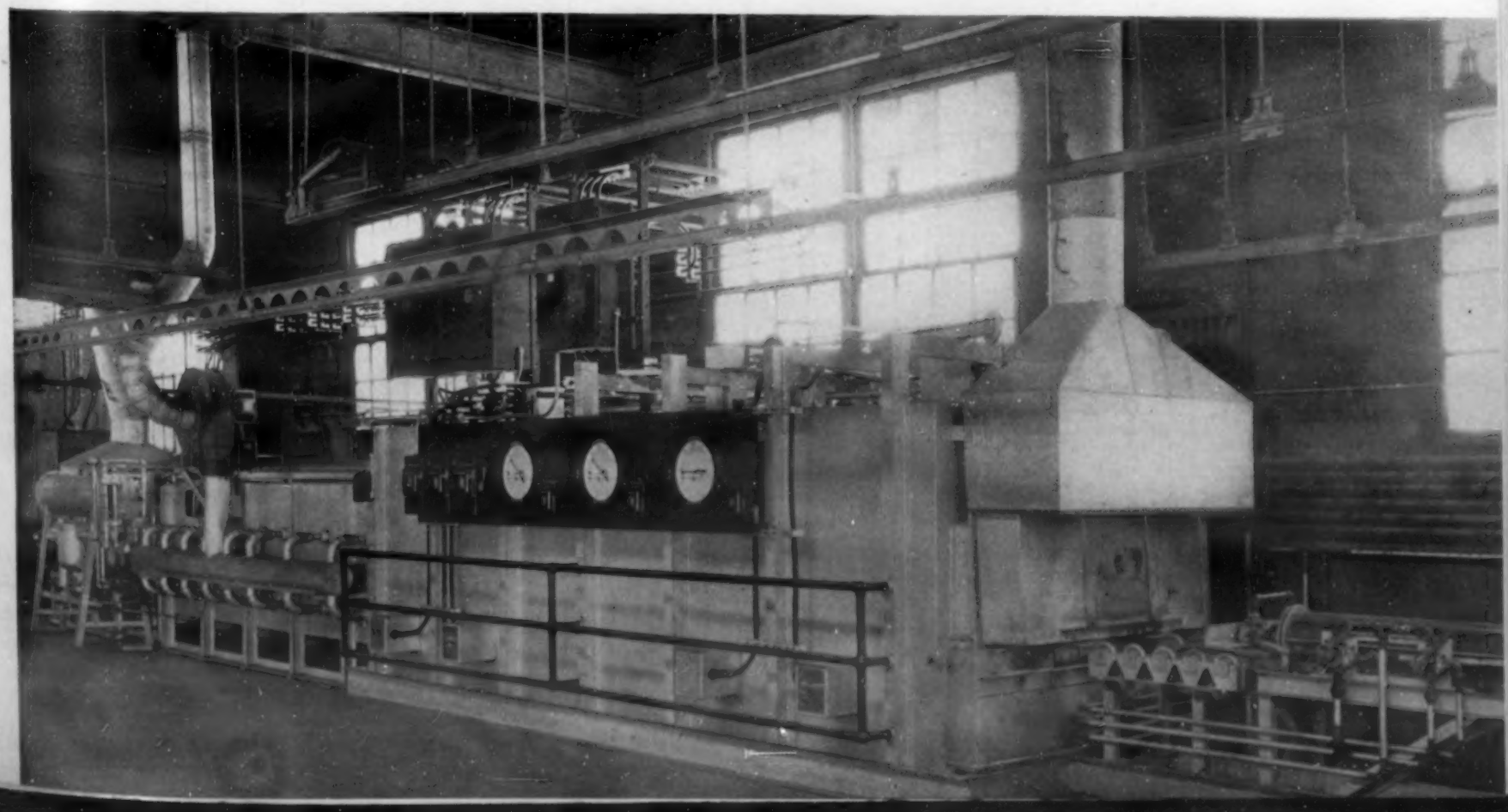
The curve for 1.2 CO, 0.3 H_2, Fig. 46, is of considerable interest. A very minute addition of CH_4 or other hydrocarbon should remove the very slight tendency toward decarburization. This gas was produced by passing air over heated iron, plus a little carbon. All reactive oxygen

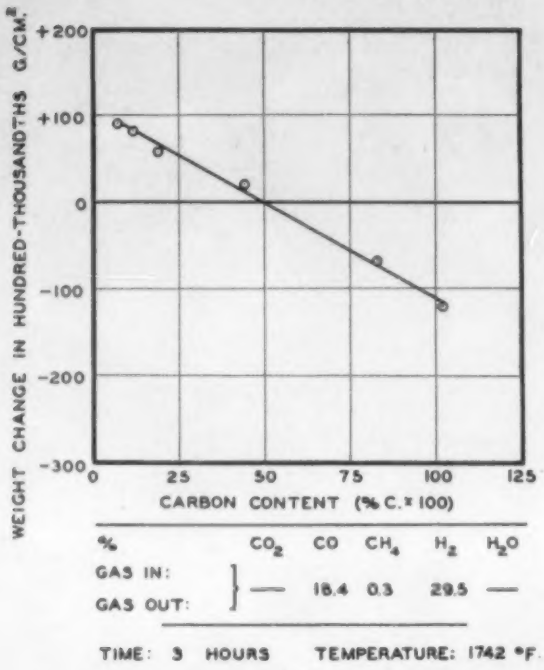


A Controlled Atmosphere Furnace for Heat Treating Steels. (Courtesy: Mahr Mfg. Co., Minneapolis, Minn.)

has combined with the iron. The oxygen in the moisture of the incoming air has reacted, freeing a corresponding amount of H_2. Gas of this type is produced about the steel when steel is packed in pots or tubes with plenty of cast iron chips. The oxygen of the air and of the moisture initially present are chiefly converted to iron oxide, while a part forms CO. Moisture is decomposed and H_2 freed. Packing in cast iron chips is an acceptable means of protection of steel surfaces in batch heating of small lots. For example, Fig. 47 shows the behavior of an atmosphere made by passing air over hot cast iron borings, and a drying train which included soda-lime. The samples were bright and

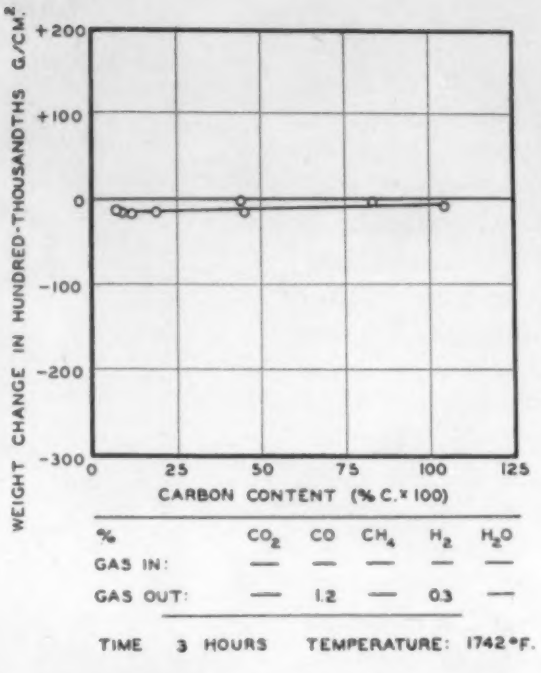
A Pusher-Type Tray Furnace for Annealing Castings in a Protective Atmosphere. (Courtesy: General Electric Co., Schenectady, N. Y.)





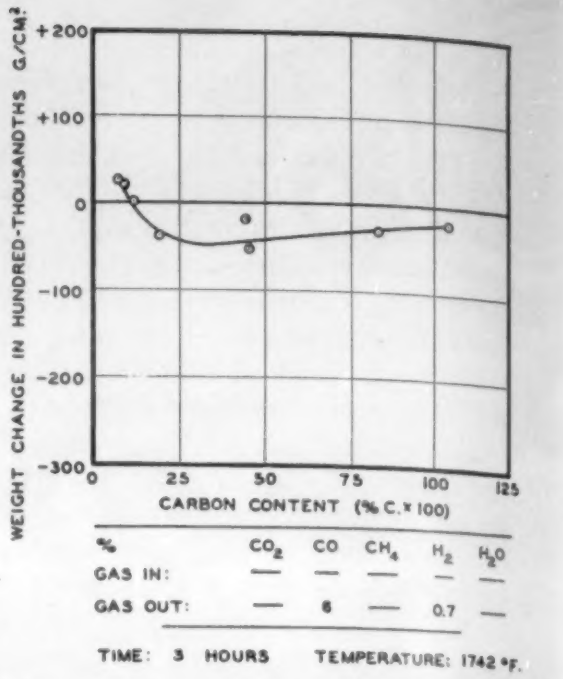
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	18.4	0.3	29.5	—
GAS OUT:					

TIME: 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	—	1.2	—	0.3	—

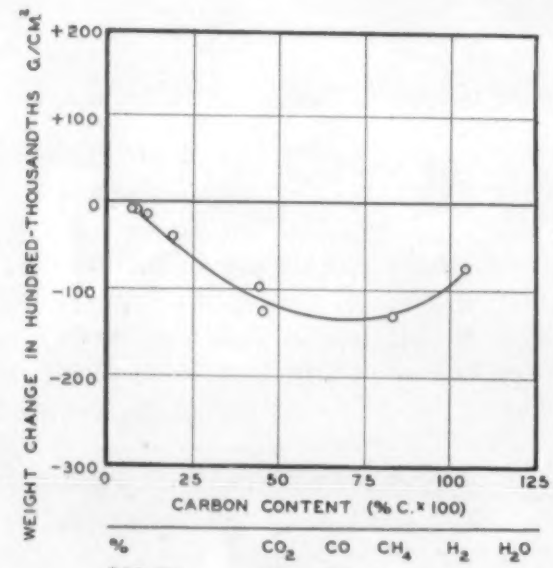
TIME 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	—	6	—	0.7	—

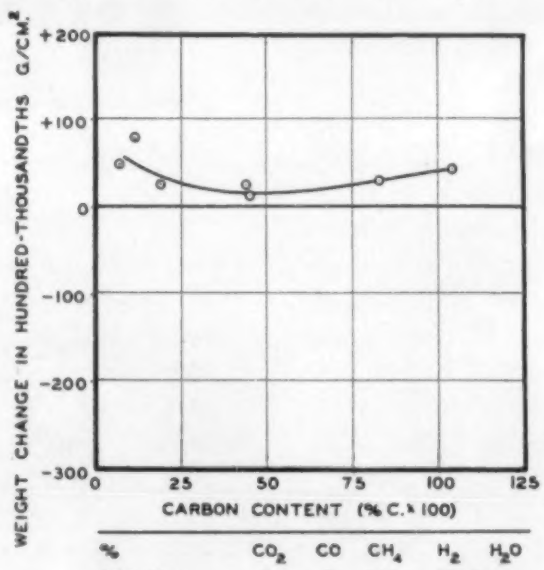
TIME: 3 HOURS TEMPERATURE: 1742 °F.

Fig. 45 (Left) Action of a Partly Burned Natural Gas Which Had Been Dried and Passed Over Hot Carbon for Carbon Dioxide Removal. Samples bright. Fig. 46 (Center) Action of an Atmosphere Produced by Passing Air Over Hot Iron, Plus a Little Carbon. The H_2 comes from the moisture in the air. Samples bright. Fig. 47 (Right) Action of an Atmosphere Produced by Passing Air Over Hot Cast Iron Borings, Drying the Resultant Gas and Removing any Traces of Carbon Dioxide Present with Soda Lime. Samples bright.



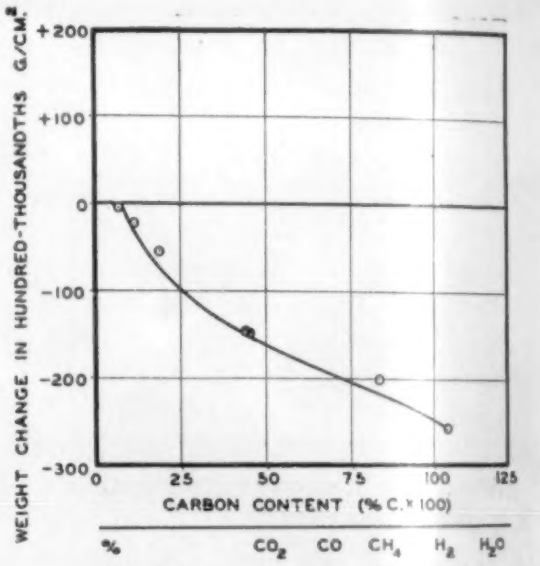
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	—	—	—	—	—
GAS OUT:	0.9	15.5	—	—	—

TIME: 3 HOURS TEMPERATURE: 1742 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	6	7	14.5	10	—
GAS OUT:	5	8	12.5	14	20

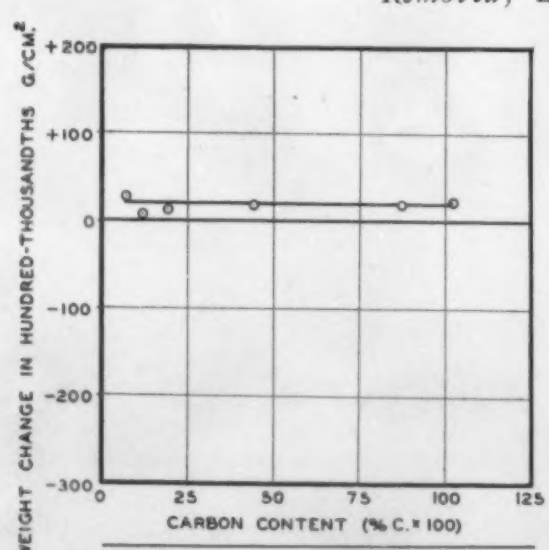
TIME: 0.25 HOURS TEMPERATURE: 1562 °F.



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	5	9	13	14	—
GAS OUT:	3	14	6	28	16

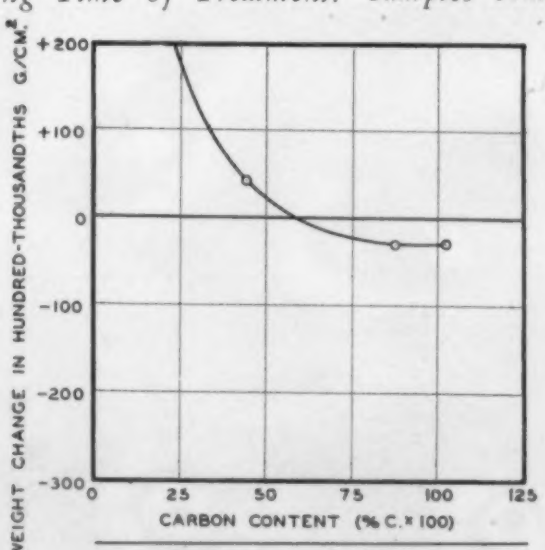
TIME: 3 HOURS TEMPERATURE: 1742 °F.

Fig. 48 (Left) Action of an Atmosphere Produced by Passing Air Over Regenerated Cast Iron Borings. Samples slightly stained. Fig 49 (Center) Action of a Partially Burned Natural Gas Atmosphere Which Has Had No Moisture Removed; Short Time of Treatment. Samples scaled, 0.45 per cent C. and higher carbon steels decarburized, loss of weight overshadowed by scaling. Fig. 50 (Right) Action of a Partially Burned Natural Gas Atmosphere Which Has Had No Moisture Removed; Long Time of Treatment. Samples somewhat scaled.



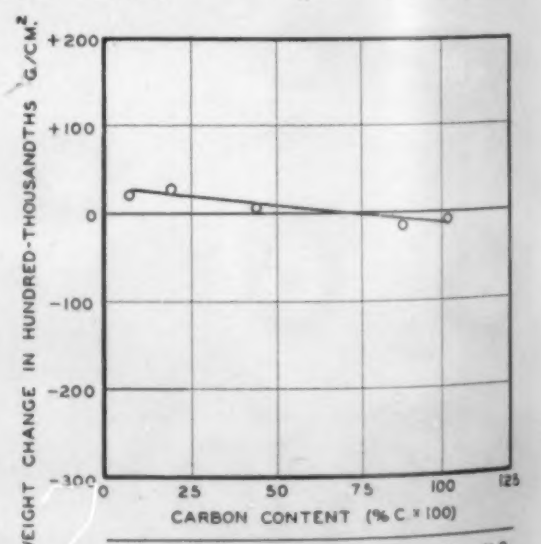
%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	3.4	15.7	8.8	87	—
GAS OUT:	2.9	15.8	6.5	66	—

TIME: 1 HOURS TEMPERATURE: 1382 °F



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	4.5	18.5	8	58	—
GAS OUT:	1.1	19.0	5.8	62	—

TIME: 3 HOURS TEMPERATURE: 1742 °F



%	CO_2	CO	CH_4	H_2	H_2O
GAS IN:	2.9	13.8	7.0	23	0.9
GAS OUT:	2.7	14.5	6.8	25	0.9

TIME. 1 HOURS TEMPERATURE: 1472 °F

Fig. 51 (Left) Effect of Using a Synthetic Commercial Atmosphere for a Short Time at a Comparatively Low Temperature. Samples stained. Fig. 52 (Center) Effect of Using a Synthetic Commercial Atmosphere for a Long Time at 1742 deg. F. Low carbon samples strongly carburized. Samples stained. Fig. 53 (Right) Effect of Using a Synthetic Atmosphere for an Hour at 1472 deg. F. Samples slightly stained.

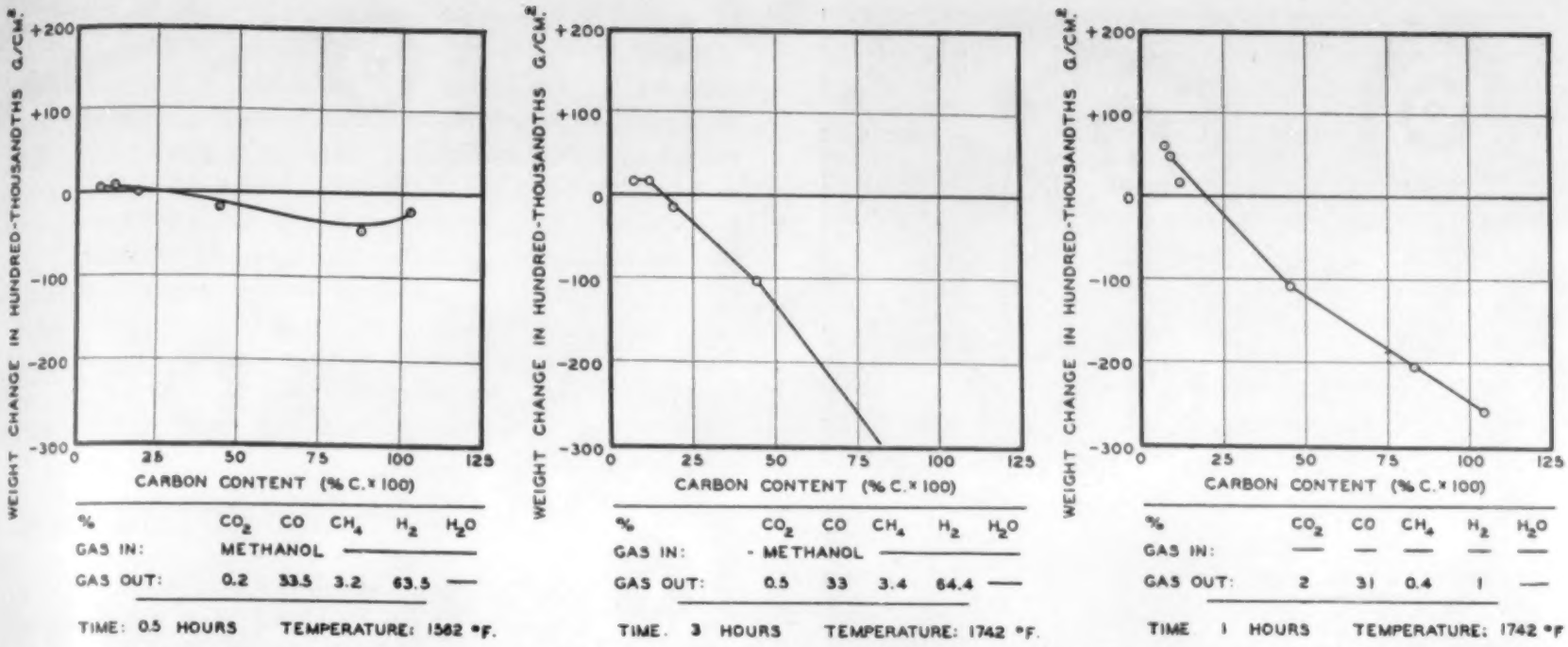


Fig. 54 (Left) Action of Methanol Vapor for a Short Time at a Comparatively Low Temperature. Samples fogged. Fig. 55 (Center) Action of Methanol Vapor for a Long Time at 1742 deg. F. High carbon samples strongly decarburized. Samples fogged. Fig. 56 (Right) Effect of Using an Atmosphere Direct from an Experimental Dry Gas Producer. Samples stained.

the results appear quite favorable. The generation of a similar gas outside the furnace and the cyclic regeneration of the iron oxide is worth considering. This was tried experimentally and the product gas was found to be rather high in CO as shown in Fig. 48. This CO probably came from the iron carbide which was formed during the reducing cycle and from deposited carbon. The samples were slightly stained in this run, possibly from the CO_2 resulting from the $CO:CO_2$ equilibrium at the temperature used. Copper or other metal that will combine readily with oxygen might prove better than iron.

Bright Hardening More Difficult Than Bright Annealing

It is plain that the problem of bright hardening is much more difficult than that of bright annealing. At the lower temperatures and on the low carbon steels normally met in bright annealing, almost any of the gas mixtures reported above might serve. With the higher carbons and higher temperatures of bright hardening, severe decarburization ensues when appreciable amounts of CO_2 or H_2O are present. For this reason, in bright hardening it is customary either to use a definitely carburizing atmosphere or one quite strongly oxidizing, since decarburization seldom accompanies the latter. Attempts to reduce scaling by increasing the CO and H_2 in a fuel gas atmosphere by raising the ratio of fuel to air, to make the gas less oxidizing without removing the CO_2 and H_2O, involve grave danger of severe decarburization. In particular, the effort to form a controlled atmosphere within a furnace muffle by burning fuel gas and air within the muffle, with the production of 10 to 20 per cent H_2O vapor, seems to involve great danger

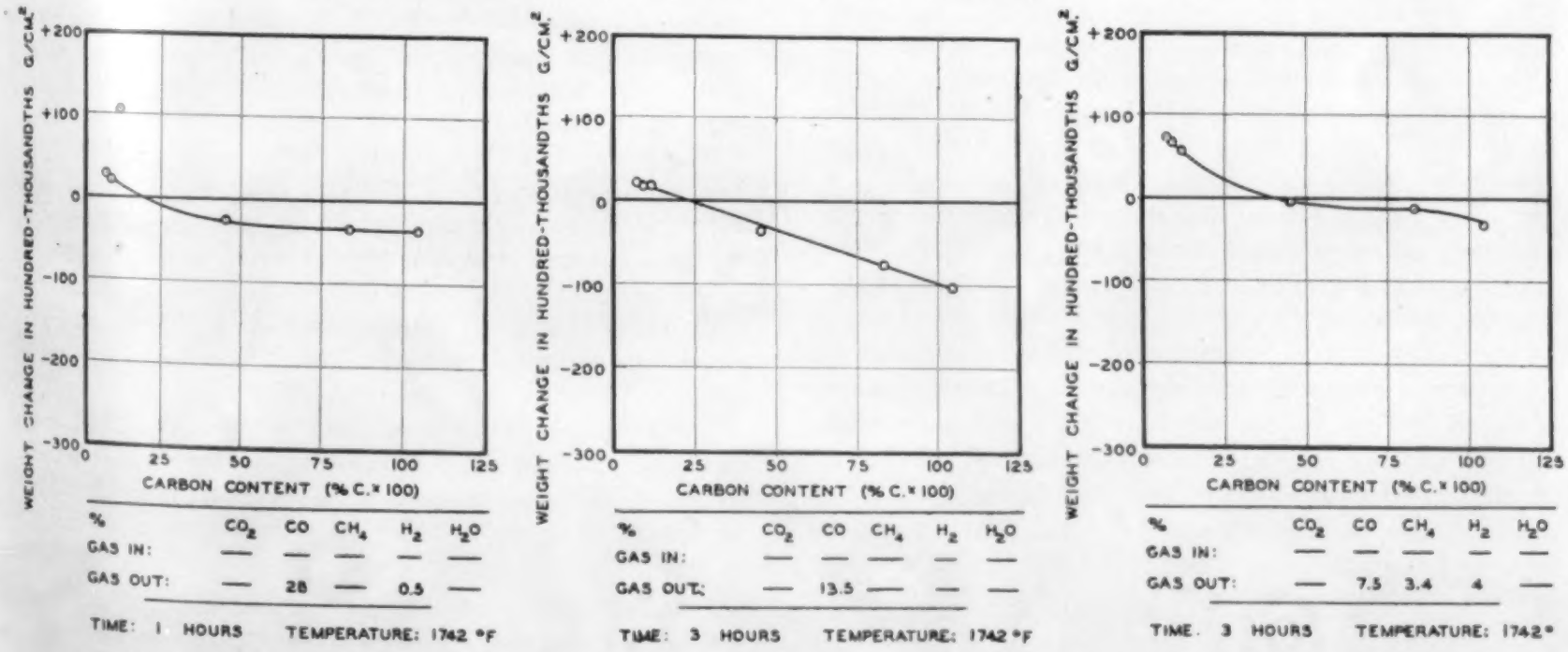
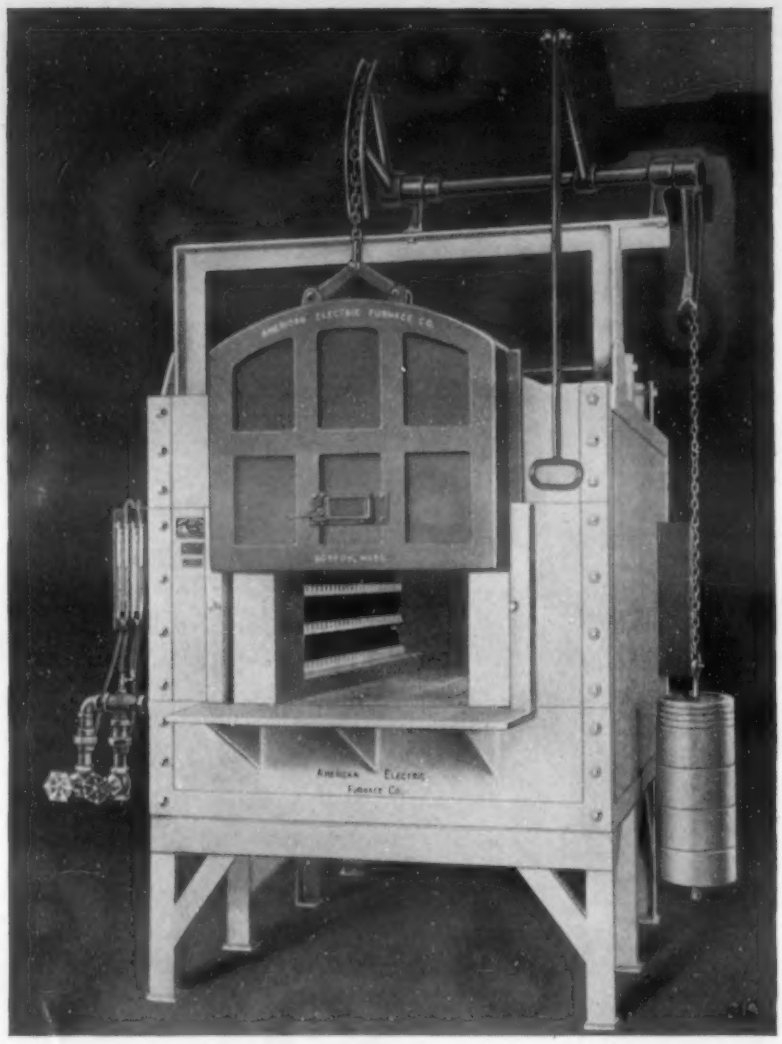


Fig. 57 (Left) Effect of Using a Purified Atmosphere from an Experimental Dry Gas Producer. Samples very slightly colored, moisture not sufficiently excluded. Fig. 58 (Center) Action of a Purified Atmosphere of 13.5 per cent Carbon Monoxide Content Made in an Experimental Dry Gas Producer. Run for medium CO content and CO_2 and HO_3 removed. Samples bright. Compare Figs. 20 and 21. Fig. 59 (Right) Effect of Adding Natural Gas to Purified Atmosphere from an Experimental Dry Gas Producer. Samples bright. Such an atmosphere could be adjusted by varying the CH_4 so as to be neutral to steel of any given carbon content.



An Atmospherically Controlled Furnace for Normal Hardening Temperatures. (Courtesy: American Electric Furnace Co., Boston.)

of serious decarburization without complete avoidance of scaling. As Figs. 49 and 50 show with an air-gas ratio of 4.3 to 1, decarburization may be largely avoided by treatment for a shorter time and comparatively low temperature but at the expense of a thin gray coat or scale and carbon deposition on the samples. The weight gain shown in Fig. 49 is due to scale—a microscopic examination showed slight decarburization on the steel of 0.45 per cent C or above. At higher temperatures and longer times decarburization becomes very severe and the samples become coated. In these runs, the H_2O content is stated as percentage of the total gas volume while the other constituents are reported on a water-free basis. Making the controlled atmosphere in a separate combustion chamber and freeing it from moisture before passing it to the furnace are becoming standard practice, for obvious reasons.

The behavior of synthetic mixtures, corresponding to some present day commercial types of furnace atmospheres is shown in Figs. 51, 52, and 53. There was some staining in these runs but they do show the type of gas needed for the higher carbon steels. Methanol has received some attention, but, as Figs. 54 and 55 show, this atmosphere tends to be decarburizing. In addition the treated samples in these runs were somewhat fogged in appearance in spite of rapid cooling.

"Dry-gas" production by passing air over hot coke or charcoal appears to be another possibility for obtaining a practical commercial atmosphere. Some work has been carried on with these atmospheres at Battelle and has indicated some of the pitfalls which may occur. Fig. 56 shows the results of a trial on one gas direct from the producer, in which the samples were oxidized and decarburized. When, however, this same type of gas was dried and passed over KOH, the severe decarburization was immediately checked though a little oxidation of the surface still occurred, as shown in Fig. 57. Fig. 58 illustrates the action of a producer gas, originally fairly low in CO, which was passed over KOH, dryers, hot copper and hot carbon. In this case the samples were bright, though decarburized. In spite of the careful purification, the gas was not as inert as those of Figs. 20 and 21 where the CO was chemically produced. The addition of methane to the type of gas, described in Fig. 58, makes the gas less decarburizing as shown in Fig. 59. These samples were quickly cooled and were bright.

CONCLUSIONS

The primary conclusion from these experiments is that for bright hardening of medium and high carbon steels without producing scale or decarburization, both CO_2 and H_2O must be avoided. This could be done either by making a gas that does not contain them originally or by removing them by suitable purification.

The CO-N_2 gases, from which CO_2 and H_2O are excluded, are suitable for a wide range of carbon steels and presumably for many alloy steels save those high in Cr. Of particular importance as a gas for practically all steels is N_2, or similar inert gas, containing only a few per cent CO which is added to assure against oxidation from infiltered air or gases carried by the work. CO is relatively inactive to carbon steels. Its slight action is reduced by dilution with nitrogen. If more than a trace of infiltered air must be combatted, more than 5 or 10 per cent CO may be necessary to prevent staining. A very slight addition of CH_4 may be used to overcome any tendency toward decarburization.

Moisture free H_2-N_2 gases, with or without CO but free from CO_2, may be used in bright hardening. While H_2 has a decarburizing effect, this can be counterbalanced and the gas made neutral by addition of CH_4 or other hydrocarbon. This addition must be regulated to fit the carbon content of the steel. As with CO, dilute H_2 such as a 5 or 10 per cent H_2-N_2 mixture is far less active than a gas high in H_2 and is much to be preferred.

The oxygen in CO_2 and in H_2O tends to be reactive with iron, while that in CO is relatively inactive. The task of adjusting a controlled atmosphere by addition of CH_4 to render it inactive is easiest when it contains (besides N_2) only CO; next easiest with H_2. Adjustment is possible with both CO and H_2 present but is very difficult and in many cases impossible when H_2O or CO_2, or both, are present.

Definitely carburizing gases, such as the cracked fuel gas or cracked oil used in gas carburizing, are suitable for some classes of work where some surface carburization may be permitted. The use of mildly carburizing gases, adjusted to give a very thin carburized surface skin, is practical for transmission gears, as an example.

Commercial gases which contain appreciable amounts of CO_2 are permissible for use on low carbon steels, but are not satisfactory for bright hardening of medium and high carbon steels. These gases are not readily adjusted by addition of CH_4 or by decreasing the ratio of air to gas in partial combustion in order to leave unburned CH_4. Either H_2 or CH_4 will react with CO_2 in the furnace to

produce H_2O with all its accelerating effect upon decarburization and its tendency to discolor the work.

It is possible that commercial atmospheres containing some CO_2 or H_2O may be made usable for bright hardening by adjustment with CH_4 when short time intervals and comparatively low temperatures are involved, but the reactivity of such gases may still make their use inapplicable because of attack upon resistors and furnace parts. While the cheapness of protective atmospheres derived from fuel gases is in their favor when the conditions of treatment are such that elaborate chemical purification is unnecessary, for good bright hardening work considerable expensive purification is indicated as being necessary. The problem of production of such atmospheres is consequently still an open one in which investigators may well look for alternative raw materials and methods of gas production. What may appear to be a costly gas may in the end prove more practical than a cheaply produced partly burned fuel gas, after considering the purification equipment necessary, the effect on furnace parts, on electric resistors and the sensitivity of the gas to a change in the character of the work.

In this report the initial phase of the general investigation on atmospheres for bright hardening has been covered, that is, information on the types of gases that will serve for use with plain carbon steels of any carbon content. Remaining phases now in progress cover the effect of the most promising gases found to date on various alloy steels and the effect upon resistors and furnace parts of the gases found most suitable for a wide range of steels.

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A LETTER TO THE EDITOR

Titanium in Pearlitic Mn Steels

To the Editor: I should like to comment on the article by Mr. Comstock in the May issue of METALS AND ALLOYS entitled "Titanium Improves Pearlitic Manganese Steels" and also on the note that Dr. Gillett has added.

It is not new to add to carbon or medium-manganese cast steels amounts of ferrotitanium corresponding to the one noted in this article. A number of foundries in the United States have for a long time been using additions of 5 to 7 lbs. per ton. The facts, therefore, seem to be that similar tests or observations have not been made before, although similar steels have been made.

The comment with regard to sulphur content and its influence upon the properties calls for further confirmation, as tests with which the writer is familiar indicate that more than 0.050 per cent S may be present without materially influencing the properties obtained.

For the heat treatment mentioned, the impact value of steel No. 3 in Table 1 is unusually high. The writer has made many tests of this composition, and finds the values under these conditions of heat treatment to be in the range of 25 to 40.

JEROME STRAUSS.
Vice President.

Vanadium Corp. of America
Bridgeville, Pa.

A CHUCKLE

The Weather and Watch Springs

From the *Columbus Citizen,* June 4—Under the heading "Blame Weather for Watch Springs That Break," appeared the following:

> Watch repairmen in Columbus had a booming business today as customer after customer appeared with watches that were stopped, the mainsprings broken.
>
> What is the cause? Not an earthquake. Nor can rough usage be blamed in most cases, according to watch repairmen. It is just the weather.
>
> "There are always a lot of broken mainsprings after sudden changes in temperature," said D. M. Knox of Schilling & Knox, jewelers at 3294 N. High St. "During lightning and thunderstorms, even more mainsprings go to pieces."
>
> "Watch manufacturers say these weather conditions cause the steel in mainsprings to *crystallize,*" explained Arthur Schmitz, watch repairman at Harrington Co., Jewelers at 84 N. High St. (Italics ours.)

The garage mechanic's terminology has been adopted by the jewelers. We doubt if the watchmakers themselves use this phraseology. Corrosion-fatigue ought to be at least as mouth-filling as "crystallization." (From R. E. Christin.)—H.W.G.

Wear of Metallic Surfaces

by E. E. LeVan

Haynes Stellite Co.,
Kokoma, Ind.

ALTHOUGH IT IS GENERALLY ADMITTED that the loss from the corrosion of metal amounts to many millions of dollars annually, few estimates are ever made of the annual loss caused by the wearing out of metallic parts. It is difficult to venture such an estimate but, from every indication, the loss is very considerable. Evidences of the staggering cost for the replacement of wearing parts confront us every day.

The necessity for overhauling one's automobile engine and grinding the valves, is obvious to everyone. More remote to many, but still very real to plant managers, superintendents, and foremen is the necessity for reconditioning industrial equipment. For instance, in the excavating and mining industries, dipper bucket teeth, chain sprockets and links, and tractor treads are but a few representative parts which require frequent attention. The wear of dies, cams, shear blades, and rolling mill parts creates an ever-present problem in steel mills. Even the farmer's plowshares, cultivator sweeps and harvesting equipment are a constant source of worry and expense.

Definitions of Wear

A few years ago, an editorial[1] in one of the leading metallurgical journals carried a statement to the effect that the most embarrassing question a metallurgist could be asked was how a given alloy would respond in service involving repeated alternation of stress, wear and corrosion, at high temperatures. The editorial continued, "We probably know less about the mechanism of wear, or how to test the wear resistance of a metal than we do about any other kind of severe service." The statement is undoubtedly still true.

The mechanism of wear involves such a large number of interdependent factors that single isolated tests can rarely approximate service conditions. Many devices for determining the wear of metals have been designed and used, but it is usually admitted by the designers that the results of these specific tests show only the resistance of the metal under test to the limited wearing conditions imposed by the testing machine.

Wear has been defined by L. Jordan[2], formerly with the U. S. Bureau of Standards, but now assistant secretary of the A.I.M. and M.E., New York, to be "the unintentional removal in service of the surface of a metal, through the action of frictional forces." Wear was thus distinguished from grinding, polishing, lapping, or "wearing in," in that all these latter involve intentional removal of the metallic surface.

Fig. 1—Dipper Buckets, Such as These, Fabricated from Manganese Steel, Last Far Longer than Those of Plain Carbon Steel.

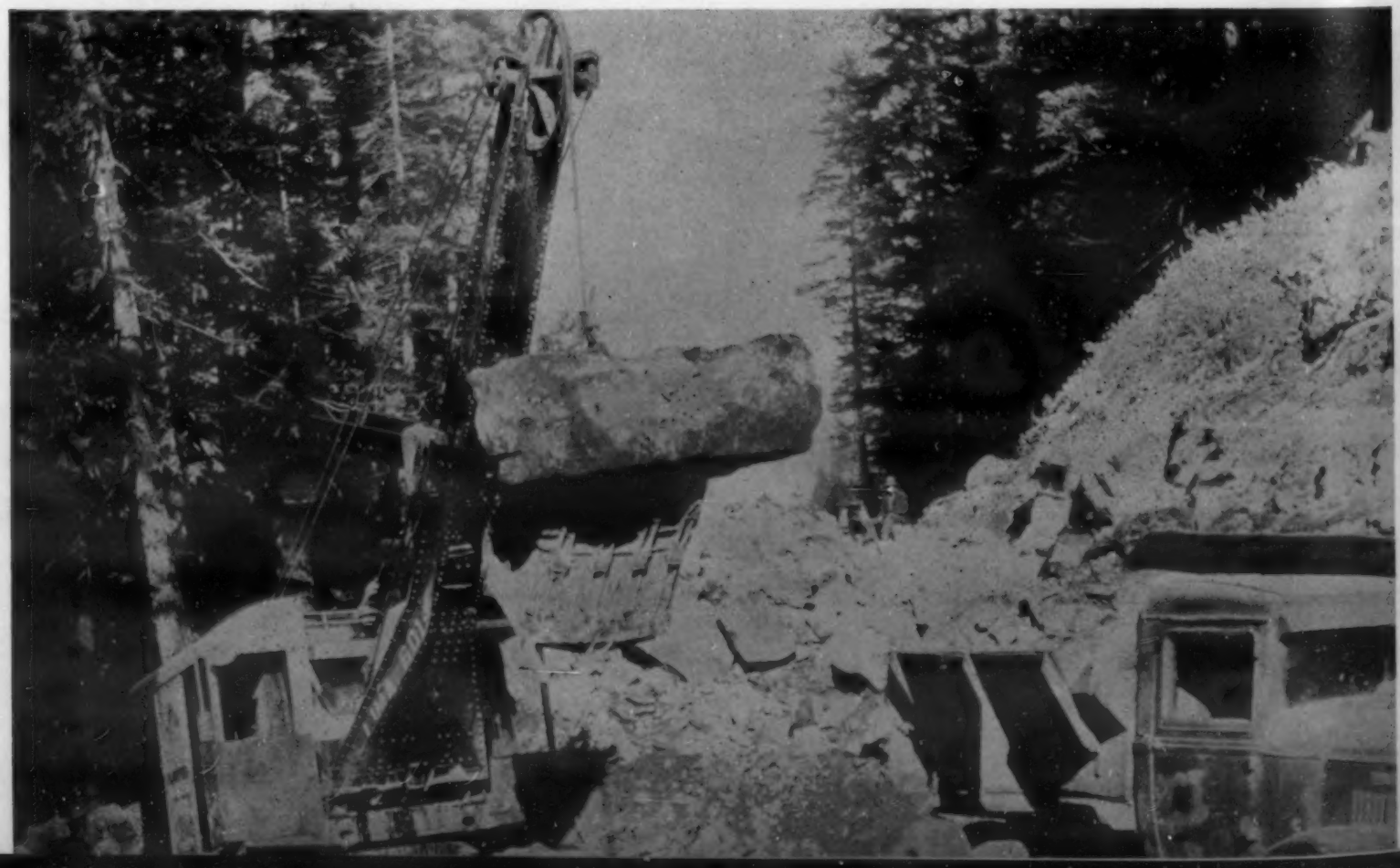

Fig. 2.—Mine Drag Scrapers Wear Rapidly Unless Protected by Special Alloys. Note the welded-on bead of a chromium-manganese-iron hard-facing alloy.

Mr. Jordan goes on to say that there are at least three commonly recognized types of wear: Wear by abrasion, by erosion, and by galling. These three types of wear are defined in this way:

> *Wear by abrasion* involves the mechanical distortion of the suface layers of the metal, followed by the removal of the distorted layers by frictional forces. Such forces are generally restricted to those developed between the wearing metal and solids.
>
> *Wearing by erosion* probably involves an alteration of the surface layers of the metal by chemical attack, followed by the removal of metal or of the products of chemical reactions by frictional forces. Such forces are restricted to those developed between the wearing metal and flowing gases, liquids or vapors.
>
> *Wear by galling* involves the adhesion or cohesion of localized areas of two bearing surfaces of metal, followed by the tearing out of small fragments from the one surface or the other, as relative motion between the two bearing surfaces continues or is initiated.

In each of these three types of wear there are two stages: First, some sort of mechanical or chemical modification of the metal surface; and second, the actual removal of material from the wearing surface.

Most wear probably results from a combination ot two or, perhaps, all three of these types, rather than from only a single one. Thus, pure abrasion may be exemplified by the initial rapid wear of two finish ground metal surfaces which are actually relatively rough if viewed through a microscope. After the intial "wearing-in," in which the abrasion produces surfaces free from the irregularities of machining, wear may continue at the same, or a slower or faster rate, by combined erosion and abrasion.

When there is occasion to speak of the wearing away of a metal by jets of steam or other fluids which are relatively free of solid particles, or of the "cutting" or "wire-drawing" of valves and valve seats by flowing liquids or gases, there is little hesitation in calling the resulting wearing action "erosion." The erosion of metal is very similar to the erosion that takes place in the forming of a river bed.

When surfaces, such as those of steel poppet valve heads and seats, are roughened after periods of use involving alternate contacts under pressure, followed by separation, small particles sometimes appear to have been picked out of one surface and rather firmly attached to the other surface. This is the type of wear which is generally known as "galling."

Hardness and Toughness as Factors

General considerations lead one to believe that both hardness and toughness have undoubtedly an important influence on the relative rate of wear under certain conditions. Extreme hardness is indication of the great resistance of the material against penetration, tearing, or the dislocation of surface particles, as manifested by the slight impression made by a steel ball or a diamond point under high pressure—such as the testing point of a hardness measuring machine. On the other hand, toughness has a tendency to reduce wear by making the separation of particles more difficult. Hardness may be conditionally taken as an index of resistance to wear by abrasion, and

toughness an indication of resistance to wear by galling. As a rule, however, resistance to wear does not depend alone on the strength of the material or its hardness as determined by one of the commonly used methods. Determination of hardness alone, especially at ordinary temperatures, is not sufficient to disclose the resistance of the material against wear.

Constitution and Homogeneity Are Factors

Some of the other factors which have a definite, essential influence on wear are the metallographic constitution and homogeneity of the material, and, of course, the pressure, speed, coefficient of friction, lubrication and initial smoothness of the wearing surfaces. Probably the commonest cause of wear is rolling or sliding friction without sufficient lubrication.

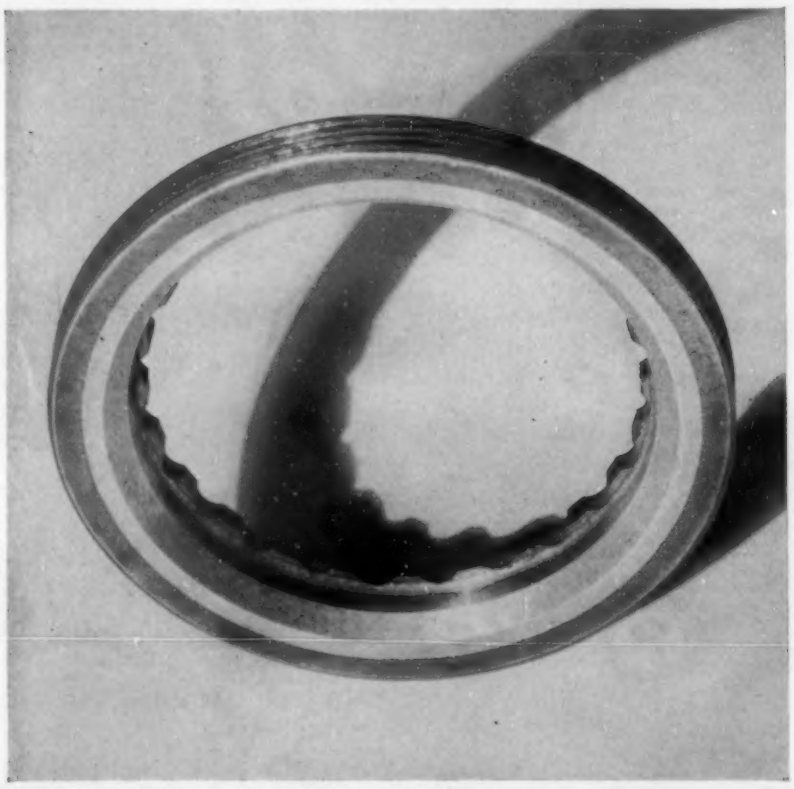

Fig. 3.—A Typical Valve Seat Insert Hard-faced with Cobalt-chromium-tungsten Alloy.

With these factors in mind, N. N. Sawin devised an instrument for measuring the rate of wear of gages and tools. The instrument consists of a revolving tungsten carbide disk pressed directly against the work which is to be tested. This type of test involves only wear caused by direct rubbing or abrasion. It gives no direct index of a metal's resistance to either galling or erosion.

Results with Sawin's Apparatus

Sawin found that most metallic materials, used by merit of their hard surfaces, should be divided into four classes:

I. The heavy metal carbides, such as tungsten, tantalum and molybdenum.
II. Hard non-ferrous alloys as, for instance, Haynes Stellite.
III. Hardened alloy steel, such as tool steel.
IV. Hardened plain carbon or case hardened steel.

For these groups, the ratio of wear in terms of the amount of metal removed in a given time can be expressed by the following mean values: I : II : III : IV = 1 : 15 : 25 : 40.

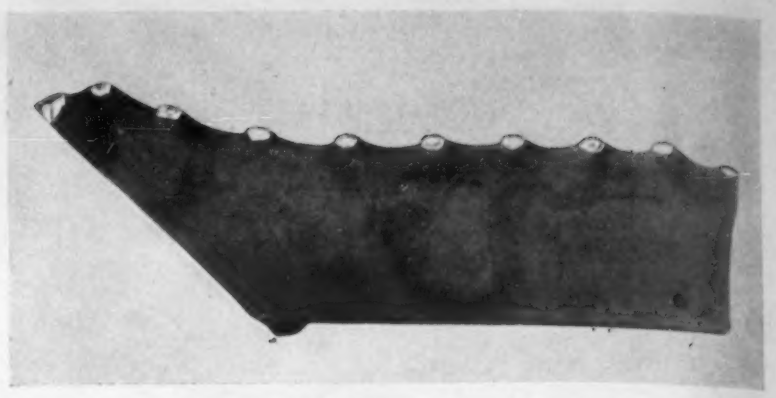

Fig. 4.—Note the Relative Wear of Material on this Steel Plowshare; Protected by a Non-ferrous Alloy Only in Spots, it Plowed 15 Acres of Sandy Missouri Soil.

Thus, gages surfaced with tungsten carbide wore only 1/25th as fast as tool steel gages subjected to a standard heat treatment.

Practical tests have also proved the verity of such a classification of materials according to their abrasion resistance. In the experience of oil well drillers this has been very evident. A little over 10 yrs. ago, when hardened tool steel bits were in use, 84 shop dressed and tempered fishtail bits were required to complete a well. The introduction of bits hard-faced with the non-ferrous alloy, described in Class II above, resulted in cutting this requirement to 44 bits; today, wells are drilled through the same formation, to the same depth with only 14 bits which are hard-set and hard-faced with inserts and crushed particles of tungsten carbide. Although the wear-resistance ratios in practice are not exactly the same as those determined by laboratory tests, the general order of magnitude is the same. The ratios of the wear resistance determined by the test method are not definite

Fig. 5.—A Hard-faced Bottom Die for Stamping and Forming Grease Cans. These Dies Last Four Times Longer Than Those of Former Materials.

Fig. 6.—With Cast Inserts of Tungsten Carbide Embedded in it, and Similar Material Crushed and Welded on to its Surface, this Oil Well Bit Drilled an Average of 50 ft. per hr. for 60 hrs. Continuously.

enough, as yet, to insure that this property in a metal, as predetermined by laboratory tests, will evidence its true economy in an actual, practical case.

The matter of predetermining the most suitable metal for a certain type of use is probably the most important result to be attained from machines designed to measure wear resistance. Such machines are a valuable aid to the engineer, but actual performance tests are always required to prove any particular choice of metal for a specific application.

Valves and Valve Seats for Autos

A case of general interest is the recent improvement in automotive valves and valve seats. A wear-resistant metal was needed to provide automobile owners with valves which would seldom or never require regrinding.

Let us first list the properties which are required in a metal to fulfill this requirement. The metal primarily must not scale or oxidize under the heat of the exhaust gases. Neither should it soften appreciably at the working temperature. Moreover, it must be strong, smooth, unattacked by the chemical action of the corrosive products of combustion of treated gasolines. It must neither pit nor pick up hot carbon particles which may be loosened, at the time of combustion, from the cylinder walls or head. And, in order to minimize galling, the seating surface should have a low coefficient of friction.

It was a large order, to be sure, but with the wide selection of metals, provided by modern metallurgical engineers, little trouble was had. Probably the first directional hint given by the list of required properties was that of strength, hardness and toughness under heat. The lower melting point metals were soon eliminated. The plain carbon steels begin to soften at the required temperature of about 800 deg. C. The higher alloy steels seemed to be almost what was desired, but proceeding down the list of wear-resistant materials still further, it was found that certain non-ferrous alloys proved to be even more suitable.

A Co-Cr-W Alloy for Facing

One of these, an alloy of cobalt, chromium and tungsten, has now been very successfully used for several years in heavy-duty engines as a valve seating surface material by manufacturers of buses and trucks. Recently, after proof of the good service of this alloy by many bus and truck lines, several large taxicab companies have standardized on "hard-faced" valve seat inserts. The operation of "hard-facing" is done by applying the alloy by the oxy-acetylene welding process to the seating surface.

Probably the most remarkable property of this non-ferrous alloy is the fact that it is not only very hard at temperatures approaching red heat, but it is actually even tougher at those temperatures than it is when cold. It is for this reason that the use of this material as a "hard-facing" on metal surfaces for protection from wear has become a standard practice in many industries.

As Sawin says, "many investigators have found that, only when materials of equal chemical analysis and identical heat treatment are compared, may hardness be considered as a sign of resistance to wear." He goes on to say that it is not possible to judge the relative resistance to wear of essentially different materials by comparing their hardness numbers. However, more and more is there a feeling that any material's resistance to wear may be effectively evaluated by a study of the hardness of the material at the actual working surface temperature.

The slightest amount of friction causes heat. In the case of iron-base alloys, heat may cause an actual change in the metallographic structure of the material. The iron may partially dissolve the hardening constituents in the surface layers of the metal. If this happens, the softer surface metal will easily wear away. This condition is undoubtedly one of the major factors involved in wear caused by sliding friction. On the other hand, hard non-ferrous alloys, not being subject to this solvent action of iron, retain the same metallographic structure during the entire temperature range below their melting points. As might be expected, their wear resistance is practically as great even at high red heat as it is when the alloys are cold. Although softer when cold than hardened high carbon steel is at room temperature, the cobalt-chromium-tungsten alloys are much harder at higher temperatures, since the heat materially reduces the hardness of the steel, while the hardness of the non-ferrous alloys remains practically constant.

With these facts in mind, it is quite possible that the wear resistance of a metal against abrasive action is directly proportional to the hardness of the metal at the temperature to which friction raises the working surface.

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"The Alloys of Iron and Carbon"

A Book Review—Plus the Reviewer's Comments on Some Moot Points

by O. W. Ellis

Director Dept. of Engineering and Metallurgy, Ontario Research Foundation, Toronto, Canada.

THE LATEST ADDITION to the series of monographs, written under the direction of the Iron Alloys Committee of the Engineering Foundation, is a contribution by Battelle Memorial Institute, prepared by Samuel Epstein. It is entitled "The Alloys of Iron and Carbon. Vol. I—Constitution," and contains 476 pages, 40 of which are devoted to a bibliography of the literature from 1890 to date. It sells for $5.00 and is published by McGraw-Hill Book Co., New York.

The new volume is attractively bound in the blue cloth which distinguishes the others of this series. The type is from the same font as that used in printing the earlier volumes; it is pleasing to the eye, and lends itself to ready reading.

The book opens with a brief discussion of the effects of elements other than iron and carbon on the alloys which are its subject and of the influence of such variables as microstructure, process of manufacture, etc. on the properties of steel and cast iron.

Approximately one-third of the book is devoted to the iron-carbon diagram. A description of the methods used in determining the points upon which the diagrams of this system are based is followed by a concise treatment of the properties of the phases, iron and iron carbide, and a presentation of the general features of the iron-iron carbide diagram. Two chapters are devoted to a study of the data upon which a selected iron-iron carbide diagram is based. The last chapter of this group of four is devoted to a study of the material upon which a selected double diagram (iron-iron carbide and iron-graphite) is based.

This work is well done, and the conclusions are presented clearly and without prejudice. Some of the photomicrographs which illustrate these chapters leave something to be desired in the way of clearness, largely because they are reproductions, not apparently of original photographs, but of other reproductions; this fortunately does not detract from their usefulness in emphasizing the points brought out in the text.

Two well-written chapters—one on the fundamentals of the hardening of the alloys of iron and carbon, and one on the effects of tempering upon the structure and properties of the hardened alloys—follow the first group of four.

Chapter VIII deals with the structure of iron and steel, and in it, among other things, is discussed at some length the appearance of the microstructural constituents of iron and steel. The discussion of these is well balanced, though certain important matters, referred to below, are given somewhat scant notice.

Heat-treating practice in general and the effects of mass and of furnace atmosphere on heat-treated steel are the subjects of Chapter IX. Rather more stress should have been placed, perhaps, upon the importance of steam and carbon dioxide in furnace atmospheres, the effects of these compounds being far too lightly dismissed in most current discussions of the practical applications of specific atmospheres.

Heat-treating operations—quenching, tempering and carburizing—form the background for Chapter X.

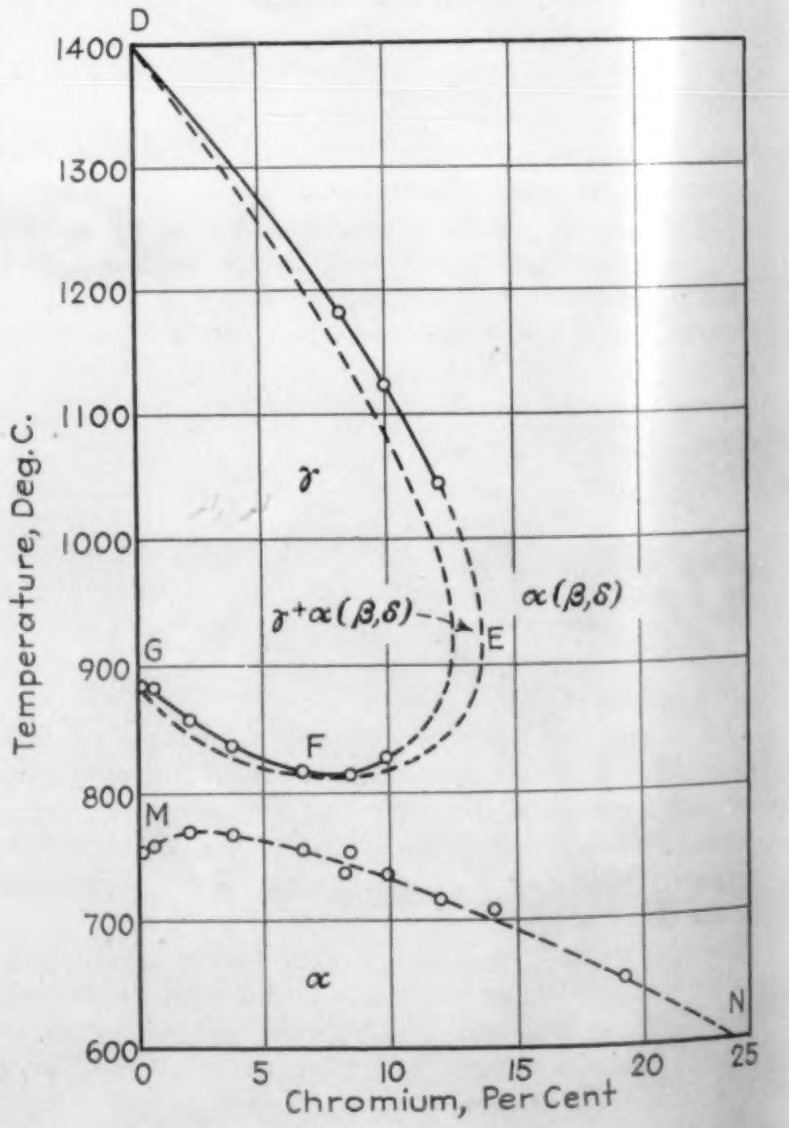
The book closes with a consideration of the effects of inhomogeneities of various types on the properties of the ubiquitous materials which are the subject of the monograph.

Many times before today has the reviewing of a book been made the excuse for hobby-riding, and the present reviewer, being thus in good company, feels urged to mount a few hobbies of his own, not to chasten the author (who, in view of the many differences of opinion about the metallography of iron and steel, has handled his subject admirably), but rather, while spurring the hobbies, to suggest alternatives to statements in the book.

On page 33, ff., the author deals with the crystal structures and temperatures of transformation of metallic iron, and in line with most, if not all, of those who have preceded him on this subject, uses the terms "alpha," "beta," "gamma," and "delta" to describe the forms of iron. The reviewer has elsewhere suggested that the time has arrived, when for the sake of clearness, these terms may well be discarded, and the desirability of such a change is not less apparent after reading the author's discussion of "The Question of Beta Iron" (Sec. 30 of the monograph).

The reviewer would observe that there are two crystalline varieties of iron—"body-centered cubic" and "face-centered cubic"—and would suggest that these be referred to as "body-centered iron" and "face-centered iron," respectively. That body-centered iron undergoes magnetic transformation at A_2 need cause difficulty neither in description nor in definition. One need only say, for example, that body-centered iron changes on heating from the ferromagnetic to the paramagnetic state at A_2. Iron, when ferro-

Fig. 1—From a Paper by Krivibok and Grossmann on "A Study of the Iron-Chromium-Carbon Constitutional Diagram," Trans. A.S.S.T., Vol. 18, p. 760, 1930. Figure Originally Due to Esser.



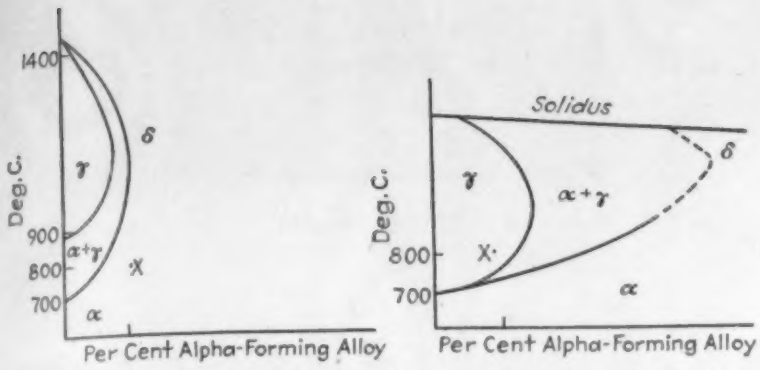


Fig. 2—From Paper by Kinzel on "Nondeforming Alpha-Delta Carburizing Steel," Trans. A.S.S.T. Vol. 19, p. 438, 1931-32.

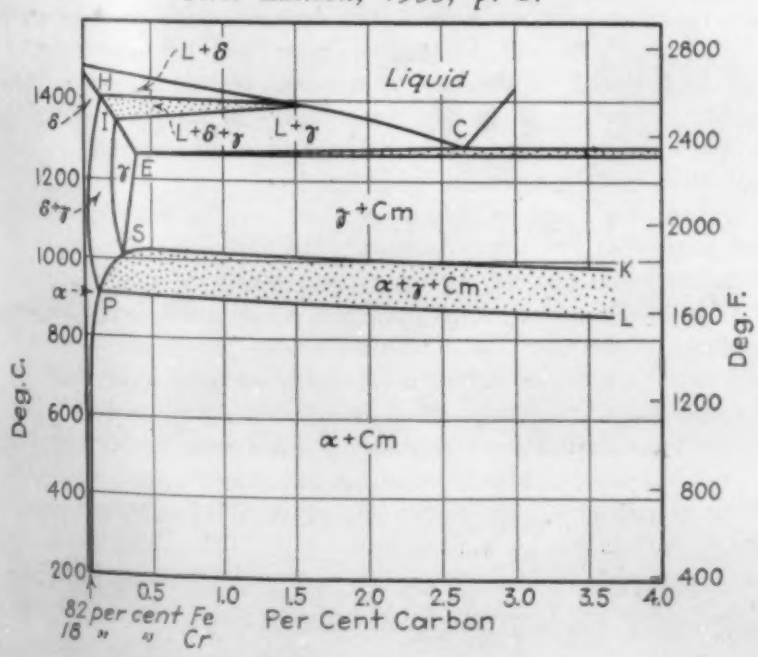
magnetic, might be described as "ferromagnetic body-centered iron"; iron between A_2 and A_3 might be described as "paramagnetic body-centered iron." It is agreed that these terms are longer than those now in use, but they are precise, and surely precision is most desirable. In writing and printing, the shorter forms "b-c. iron" and "f-c. iron" could be used.

The confusion resulting from the use of the terms "alpha" and "delta," for example, is well exemplified in diagrams which have illustrated numerous papers during the last few years, and of which Figs. 1 to 4 of this review are interesting examples. How much clearer and more precise it would have been, had the captions "b-c." and "f-c." been used in place of the Greek letters α, δ and γ, respectively, in Figs. 1 to 3, and the term "body-centered iron in place of the contradictory description "Delta (or α) iron" in Fig. 4? And how much less confusing would have been the title "Non-deforming Body-centered Carburizing Steel" than the title "Non-deforming Alpha-Delta Carburizing Steel" for the paper by Kinzel, from which Fig. 2 of this review was taken?

As already mentioned, Section 30 of the monograph deals with the question of beta or (to use the more descriptive name suggested by the reviewer) paramagnetic b-c. iron. The author here observes: "John Johnston remarked that Heisenberg's theory of ferromagnetism offers an explanation which, though incomplete, is in many ways satisfactory. McKeehan has briefly discussed Heisenberg's theory. The magnetic transformation (A_2) seems to represent an energy change *within the atom*." The reviewer has italicized the words "within the atom" in the sentence last quoted, because he is of opinion that they offer a clue to the correct disposition of the A_2 line in the iron-iron carbide and iron-graphite diagrams.

Epstein, in Section 49 of his book, discusses the disposition of this line at considerable length, concluding that the logical procedure is to indicate the magnetic change points as following OSK in the diagram.

Fig. 3—From "The Book of Stainless Steels," by Thum, First Edition, 1933, p. 8.



What still puzzles the reviewer is that a change occurring *within* the atoms of iron should be influenced so remarkably by the atoms of carbon as apparently it is—to judge by the A_2 line in Epstein's selected diagram (Fig. 15, p. 96). The atoms of iron in an alloy containing, say, 0.43 per cent of carbon are presumably the same in nature as, though less in number than, those in an alloy containing, say, 0.03 per cent of carbon. The A_2 point, according to Epstein's selected diagram, occurs at the same temperature (770° C.) in the 0.43 per cent, as in the 0.03 per cent, carbon alloy, but at a temperature 47 deg. C. lower in the 0.83 per cent carbon alloy—the eutectoid (Fig. 11, p. 84). Thus, whereas an increase in carbon from 0.03 per cent to 0.43 per cent is without apparent effect upon the *internal configuration* of individual iron atoms, an increase in carbon from 0.43 to 0.83 per cent causes a change so marked as to lower the Curie point by 47 deg. C. An equally remarkable phenomenon is the persistence of the Curie point at 723 deg. C., despite further increase in carbon content from 0.83 per cent to 6.68 per cent.

Why should the effect of carbon be discontinuous? Why, for example, should not the effect of carbon upon the *internal configuration* of the iron atoms be proportional to its amount and independent of the positions of the iron and carbon atoms relative to one another on the lattice, whether body-centered or face-centered? Were this true, in eutectoid steel and, for that matter, in all alloys containing more than 0.43 per cent of carbon, the *internal configuration* of individual atoms of iron would not be expected to change at a temperature lower than that at which it changed in 0.43 per cent carbon steel, provided that the 0.43 and 0.03 per cent carbon steels had the same Curie point. All of which, being interpreted, means that the reviewer supports Honda, Murakami, and Kinzel in their views regarding the situation of the A_2 line in the iron-iron carbide diagram.

The foregoing is not all that can be said on this subject. On page 283 of the monograph Epstein quotes d'Arcambal as stating that ". . . for a 1 per cent carbon steel, 750 deg. C. . . . is too low for commercial practice." Nevertheless, the loss of magnetism of tool steel has been, and is being, used with success in the commercial determination of its quenching temperature. The inference appears to be that tool steel does not lose enough magnetism on heating through A_1 to render a magnet ineffective in determining the temperature at which the steel should be quenched so as to be fully hardened. For all *practical* purposes, then, it would seem that for tool steel A_2 must be above 750 deg. C.—in all probability it is at 770 deg. C.—the Curie point for steels containing between 0.03 and 0.43 per cent carbon. The reviewer has no desire to be dogmatic regarding the A_2 line, but he does suggest that more work is needed to prove that it does *not* extend horizontally across the diagram.

Of special interest to the reviewer was the chapter (VIII) on "The Structure of Iron and Steel," particularly that section (97) dealing with pearlite. Therein reference is made to the work of Carpenter and Robertson on the formation of pearlite, and a figure (No. 97) is reproduced from their paper (ref. 448 in the bibliography) for the purpose of illustrating the mode of formation of pearlite from austenite. While it is true that this figure (here reproduced as Fig. 5) illustrates with reasonable accuracy what occurs when eutectoid steel is cooled through the critical range at slower and faster cooling rates, respectively, it does not emphasize sufficiently the important fact that in hypo- and hypereutectoid steel, either pro-eutectoid ferrite or pro-eutectoid cementite (as the case may be) forms at the boundaries of the austenite *prior to* the appearance of pearlite.

Epstein remarks that: "Carpenter and Robinson concluded that the formation of pearlite does not begin with the appearance of a number of parallel lamellae throughout a grain. Instead, in hypo- or hypereutectoid steel pearlite begins to form at the edge or a corner of an austenite grain, adjacent to the proeutectoid ferrite or cementite, and then spreads gradually through the austenite as illustrated" in Fig. 5 hereof. Fig. 5 most certainly does not illustrate the remarks in the sentence last quoted. What happens on cooling hypo-eutectoid steels through the critical range

is that iron atoms at various points on the boundaries of the austenite grains commence at Ar_3 to rearrange themselves on a body-centered lattice.

The reviewer has suggested elsewhere (*Trans.*, A. S. M., 1934, vol. 22, pp. 139-183) that the number of points at which rearrangement commences is closely related to the rate of cooling of the steel, being relatively few with slow rates of cooling, increasing to a maximum with increase of cooling rate, and then falling off very considerably with still higher rates of cooling—rates of cooling just short of those which in some steels will produce a Widmanstätten structure, and in others martensite. The reviewer has further suggested that with rates of cooling which result in the formation of highly developed lamellar pearlite there may be a definite relationship between the positions of the points at which ferrite starts to form at the boundaries of the austenite crystals and the distances between the lamellae of carbide which start to crystallize out when the concentration of carbon at the boundary between the waxing ferrite and the waning austenite reaches the saturation point.

Whatever the rate of cooling of hypo-eutectoid steel (so long as the critical rate is not exceeded), among the most important factors determining the structure of the pearlite formed (the word "pearlite" being used in probably its best and widest sense, to include both sorbite and troostite) are (1) the number of points at which transformation of face-centered iron to body-centered iron occurs at boundaries of the austenite grains (or, in other words, the number of points at which ferrite starts to form at these boundaries), and (2) the concentration of carbon in individual grains at the boundary between the growing ferrite and the diminishing austenite. These factors are given no consideration by the author. It is felt that the mode of formation of the various types of pearlite should not be quite so lightly dismissed as on page 258 of the monograph, and that a full treatment of this subject might well be embodied in future editions.

Yet another structure, the Widmanstätten, is dealt with rather loosely. The impression created by the author is that the Widmanstätten structure occurs only in cast steels, whereas a structure to which the term "Widmanstätten" has been applied (with, it is thought, justification) is not by any means infrequently found in forged steels which have been cooled at certain rather critical rates. Numerous failures of forged steel parts have been reported, all of which were due to the Widmanstätten structure here referred to—a structure which is associated with considerable brittleness in steel, and of which a photomicrograph is shown in Fig. 6.

What the reviewer is at pains to point out is that the Widmanstätten structure is not found in cast steels only; it may be a feature of forged steels of a wide range of compositions. Belaiew and Séférian, for example, in a recent paper on "A Study of the Widmanstätten Structure in Welds", (12th International Congress on Welding, June, 1936), have shown quite clearly that in welded materials: "The structure may be formed from an initial liquid state, as in the weld, or from *an overheated solid state*" (italics by the reviewer). As the reviewer has pointed out in his paper referred to above, the Widmanstätten structure can be caused to appear and disappear in one and the same rolled bar, according as the bar is cooled rapidly or slowly. To produce the Widmanstätten structure in steel cooled from any given temperature, it

Fig. 5—From Epstein's "The Alloys of Iron and Carbon—Vol. 1—Constitution," p. 258.

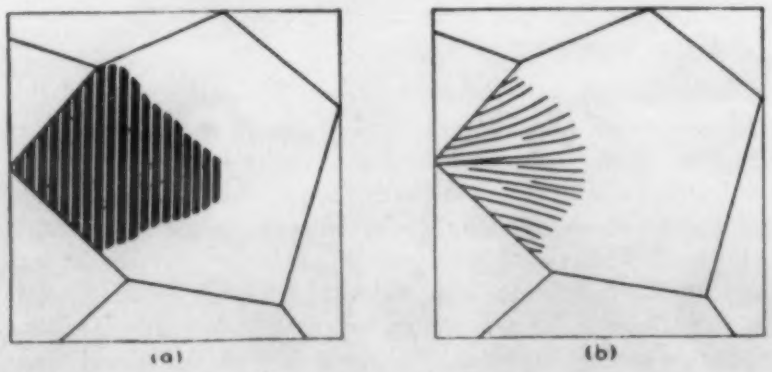


Fig. 4—Widmanstätten Structure as Found in Forged Steels Cooled at Certain Critical Rates.

is only necessary that the rate of cooling fall within certain limits. The Widmanstätten structure here mentioned is more readily produced in coarse than in fine-grained steels.

In closing, the reviewer is tempted to ask why the new system of nomenclature suggested by Marsh in his monograph, "Principle of Phase Diagrams," has not been employed by authors of books in this series published since its appearance. None realizes better than the reviewer the difficulty of adopting a new nomenclature, but it seems a pity that, having "approved for publication" Marsh's book, the Iron and Steel Committee has not required that authors of subsequent monographs use its contents. The employment, for example, of the term "tricrystic austenite" to describe the 1.7 ± 0.3 per cent carbon alloy of the iron-iron carbide system and similar alloys (austenites of maximum carbon content) would save much time and trouble. Other instances, where Marsh's nomenclature might well be used, come to mind, but cannot be dealt with here on account of space.

Comments by the Author

One must admire the enthusiasm with which Mr. Ellis has entered into this discussion. As metallurgy has matured, we have all naturally tended to become hard-headed and more absorbed in the practical. That we feel the need for theoretical thinking, however, is indicated by our conversations, which will as frequently turn to the theoretical as the practical. It is good then to see a practical man of Mr. Ellis' standing entering with relish into a written discussion of theoretical matters.

Granting the simplicity of Mr. Ellis' suggested nomenclature "b-c." and "f-c." for two forms of iron instead of the Greek letters, α, β, γ, and δ, it is hardly possible in a book to undertake changing such generally accepted usage. Such changes must be left mainly to our pedagogues; time will tell whether they will be accepted by the new generations of metallurgists. This applies particularly to the new nomenclature in Marsh's "Principles of Phase Diagrams" which would seem difficult and alien to the vast majority of present-day readers.

One of the principal values of theorizing is that it suggests and paves the way for experiment. Mr. Ellis argues from theoretical analogies that the A_2 line extends across the whole diagram and that the magnetic transformation A_2 is not lowered to the eutectoid temperature along the line OSK. The writer, however, prefers to accept the experimental determinations which indicate that the magnetic transformation is lowered along the line OSK, as has been substantiated recently by Mehl and Wells.[1]

I am indebted to Mr. Ellis for his corrections to the discussion of the crystallization of pearlite and of the Widmanstätten structure as well as for his kind review.

SAMUEL EPSTEIN

[1] R. F. Mehl and C. Wells. "Constitution of High-Purity Iron-Carbon Alloys." Tech. Pub. 798 A.I.M.M.E. 1937.

Metallurgical and Commerce News

BY THE EDITORS

Large Stainless Steel Ingot Output in 1936

Production data for stainless steel ingots by analysis for the year 1936 have recently been made public by the American Iron and Steel Institute. They are interesting. The output for 1936 as compared with the previous two years is as follows in gross tons:

Type	1934	1935	1936
"18 and 8"	19,777	24,711	39,107
12 to 14% Cr	8,902	13,232	23,598
16 to 18% Cr	8,077	12,837	21,288
All other high Cr or Cr-Ni alloys	13,161	14,917	6,973
Totals	49,917	65,697	90,966

Thus in 1936 the total production of stainless—or corrosion and heat resisting—steels at 90,966 tons is an increase of about 38 per cent over 1935 and about 82 per cent over 1934. No data were collected by the Institute previous to 1934. Whether their data represent returns from the entire industry is also not stated.

Of interest also is the marked increase last year in the production of the 18 Cr-8 Ni or "18 and 8" type at 39,107 tons of ingots. This type predominates and is the one most widely used for rolling into various products. Substantial increases are also to be noted in the plain Chromium alloy steels. The falling off in the "all other" is rather surprising.

Large Expansion in Stainless Steel Rolled Products

Statistics covering the production of rolled stainless steel products have recently been made public by the American Iron and Steel Institute for 1936. The record as compared with the two previous years is as follows in gross tons:

	1934	1935	1936
Plates	1,560	1,368	2,120
Sheets	17,076	10,816	14,973
Strip	.....	9,844	15,837
Bars	8,870	9,208	15,721
Light struc. shapes	.....	16	43
Skelp and blanks or pierced billets	40	.....	478
Wire rods	3,663	4,550	4,731
Forging blooms and billets	2,448	4,423	6,842
All other	422	1,574	620
Totals	34,079	41,799	61,365

A new record in stainless steel rolled products was made in 1936 at 61,635 tons. This is about 46.5 per cent in excess of the 1935 production and about 80 per cent over the 1934 record. No statistics were collected previous to 1934. It is not stated whether these data represent the entire industry.

It is interesting to note that the production of rolled sheets and strip increased markedly in 1936—the total of 30,810 tons is about 50 per cent in excess of the 20,660 tons for 1935.

In both cases the rapidly expanding use of rolled stainless steel products is reflected by these data.

Alloys in Furnace Construction

At a meeting some weeks ago of the Iron and Steel Engineers, M. H. Mawhinney, consulting engineer, Salem, Ohio, in a paper on "Industrial Furnace Design," gave an interesting account of the type of furnace used 15 years ago. While it performed satisfactorily under most demands at that time, it had no steel shell, insulation or controls. But phenomenal strides have been made since then to keep up with the modern requirements for heating steel. Various types of heating units running from the one-way fired circular soaking pits to the latest design in annealing furnaces were described by the speaker.

Particular attention was given by Mr. Mawhinney to the use of alloys in furnace construction. For those parts subject to stress under motion, the standard practice is to use an alloy of about 25 per cent Ni and 15 per cent Cr, while for equipment which is supported and is engaged in no movement, 12 per cent Ni and 25 per cent Cr alloy is used.

Testing Electroplated Deposits

Late information on certain phases of electroplating was the feature of the last meeting of the season of the local Metropolitan (New York) section of The Electrochemical Society. The speaker was Dr. William Blum who is head of the electro-deposition division of the Bureau of Standard at Washington. He is joint author of a text book on electroplating and a recognized authority on the subject of electrochemistry.

Dr. Blum took as his subject "The Testing and Specification of Electroplated Coatings." There is need, or has been, he said, of more precision and control in the art and of an improvement in plating methods and equipment if the highest quality and dependable results are to be assured.

Discussing the electro-deposition of metals on metals, Dr. Blum said that there are three chief points in judging plating; thickness, adherence and quality. When it comes to developing tests for these and then to preparing specifications, the problem is a difficult one. This is manifest, even to the layman. Inevitably thickness varies under the best conditions, especially on objects of irregular shape. There is what is known as average thickness and local thickness. As to adherence, this will vary with the metal to be covered or plated and with the metal to be deposited such as nickel, chromium, cadmium, silver and so on. Quality may vary for many reasons but science is regulating this, and improving and stabilizing it.

When it comes to tests and specifications, the problems are many. Dr. Blum illustrated, by concrete examples and by slides, two or three methods of testing adherence. Most of this address was directed to discussing tests for thickness and some of the methods. The chord method was explained but the most interesting test was described as the magnetic test for nickel plate. A machine developed for this purpose was explained and exhibited. With the advances, and they are many, which have been made of late years, reliable and satisfactory testing of electroplate and hence the framing of specifications are more easily accomplished.

Permanent Magnet Steels

Discussing "Permanent Magnet Steels" before one of the local sections of a large technical society recently, A. A. Hassan, metallurgist at the Atha Works of the Crucible Steel Co. of America, Harrison, N. J., first briefly reviewed the earlier steels of this type such as the tungsten and the chromium steels and also the cobalt alloy magnet steels.

His chief discussion dealt with the newer steels—the Al-Ni and the Al-Ni-Co, known as "Alnico." The modifications of this base steel by addition of molybdenum, copper, and so on were also discussed. The magnetic properties of all the steels were dealt with, showing the superiority in most cases of the Alnico type.

The method of manufacture of the Alnico type was described. The raw materials are melted in an Ajax high frequency induction furnace and the alloy poured into dry or green sand molds—all the products are made as castings. The resulting alloy is usually hard and sometimes brittle and non-machinable. Grinding is necessary to finish the product to correct shape. The heat treatment, when necessary, was discussed.

Many of the Alnico permanent magnet steels are now used in the radio industry, the telephone industry and in magnetos. They are expensive and usually sold by the piece rather than the pound. They are usually small for a greater effectiveness results from the Alnico type and hence less mass is necessary. The Crucible company is one of the largest producers of permanent magnet steels in the country. For the Alnico types, it is a licensee of the General Electric Co. which owns the patents.

Pig Iron Imports Still Large

There has been considerable talk in these New Deal days about the competition of foreign pig iron with the American product. That there is, or has been, some basis for this agitation is demonstrated by an analysis of Government statistics. This establishes the fact, as shown in the table below, that in 1936 these imports were the largest in our history but that they have declined somewhat in 1937:

Year	Tons per Month
1937 (to May 1)	11,490
1936	13,826
1935	10,911
1934	9,622
1933	13,220
1932	10,890
1931	7,038
1930	11,400
1929	12,300
1913	10,900

The present volume of over 11,400 tons monthly, according to the latest data available, is less than the record volume of 13,826 tons monthly in 1936. This is due, perhaps, to the larger demand abroad for pig iron as evidenced by our exports, but even the present imports are larger than in any year but two since 1929 and exceed the imports of 10,900 tons per month in 1913. They also are nearly 64 per cent in excess of the low point in 1931.

Our Imports of Chrome Ore

Some interesting data have lately been made public by the information service of the W. P. A. through Maurice Judd. Discussing various phases of our import statistics, particularly chrome ore or chromite, he says the following have been the imports, duty free, of this material for 1931 to 1935 inclusive in gross tons:

Year	Total	Chromium Content	Value
1931	212,528	102,716	$3,314,776
1932	89,143	43,830	1,625,733
1933	116,511	51,165	1,426,450
1934	192,297	82,969	2,227,787
1935	259,063	116,277	3,604,491

According to this table the value per ton in 1935 was about $31 but in 1931 it was $32.27 per ton. At various times in the years covered, says Mr. Judd, imports of chromite have been received from 20 countries, though in 1935, about two-thirds of the total came from French Oceania and Mozambique.

Alloy Steels in Transportation

In an address at the semi-annual meeting of the American Society of Mechanical Engineers in Detroit recently, Edward G. Budd, president of the Budd Mfg. Co., Philadelphia, said that there is practically no limit to the amount of rail travel that can be induced by improved travelling conditions. It has been demonstrated in several runs in this country that mileage can be quadrupled by giving more attractive service and lower fares and by reducing the running time betwen terminals, he contended.

In adopting lightweight alloyed steel, such as stainless steel, as a medium of construction the railroads followed the lead of the automobile and airplane, according to Mr. Budd.

The desirableness of lightweight in automobiles and airplanes has resulted in the very general use of alloyed steels, which under heat treatment have a strength and resistance to fatigue many times that of the mild steels previously in general use, he said. "These alloyed steels cost a good deal per pound, but it was found that their general use resulted in lowering of the cost of the automobile. By using alloyed steel we have cut the weight of our trains to one half or less of that of the old-type trains, at the same time maintaining as much collision strength as in the old heavy cars, because the material we use, even though much lighter, is four times as strong as mild steel, of the grade used in the old cars. We have kept the horsepower of the pulling unit high enough so that the weight of the train per horsepower is 400 lbs. or less. The older type, or what we called until recently the standard train, has a weight of from 800 to 1,000 lbs. per hp. With the decreased load we can stop and start more quickly, go up hill at the same speed we go down, and make the total elapsed time between destinations marvelously less than ever has been attained before."

Quantity and Source of Bauxite Imports

Large quantities of crude bauxite are imported into the United States yearly on which a duty of $1 per gross ton is paid. It is one of the few raw materials which is dutiable. According to Maurice Judd of the information service of the W. P. A., the imports from 1931 to 1935 were as follows in gross tons:

Year	Total	Value
1931	306,490	$1,495,577
1932	205,620	1,042,829
1933	149,548	899,696
1934	166,653	1,201,710
1935	199,959	1,448,592

In 1935 the imports of the material came from only four countries with the great bulk from two—British Guiana and Netherlands China.

Cooperation in Foundry Operations

At a joint meeting of the Quad City Chapter of the A.F.A. and the Tri-City Chapter of the A.S.M., George Zabel, foundry superintendent, chief chemist and metallurgist of Fairbanks, Morse & Co., Beloit, Wis., declared that there is a certain lack of cooperation between the engineering departments and the foundry proper. The engineer should have sufficient training for a fundamental understanding of the making of castings, cores, materials used and the different castings. The foundrymen, on the other hand, should have an opportunity to get information from the engineer.

This lack of cooperation, Mr. Zabel said, is being gradually eliminated, in his opinion, and a more mutual basis is becoming apparent in the two fields. He cited examples of how design has become important in the foundry industry, accompanied by fewer operations and less expense. Foundrymen must think in terms of exactness of measurement, design of castings, soundness, prices and materials used.

FURNACES AND ATMOSPHERES FOR

ANNEALING COPPER

WITH ELECTRIC HEAT

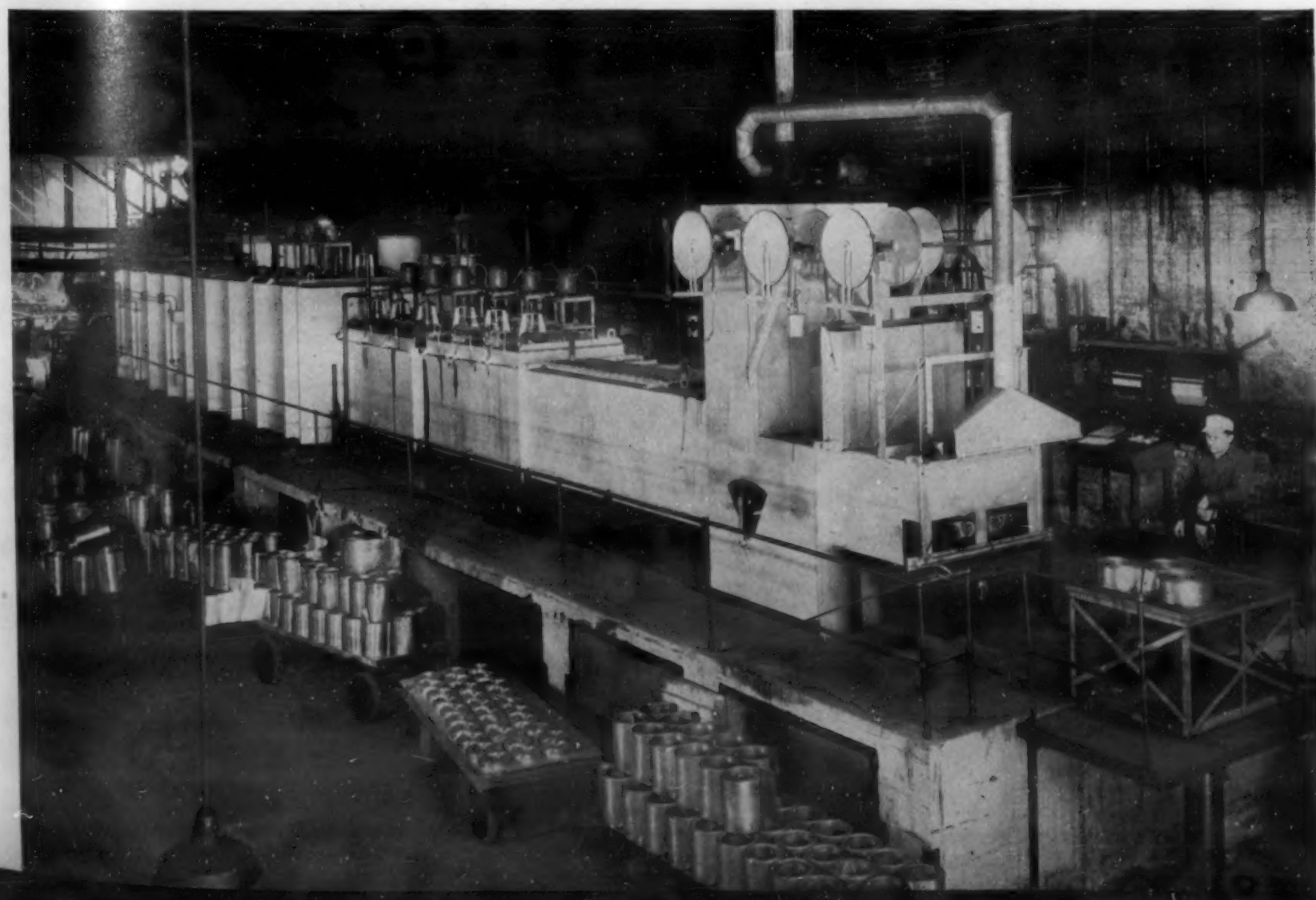
by E. K. Hansen and P. H. Brace

Industrial Heating Engineer and Consulting Metallurgist respectively
Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.

ELECTRIC FURNACES of the resistor type have long been employed for those difficult heat treatments occurring particularly in the ferrous metal industry, where uniform heating and accurate temperature control are essential to obtain a properly treated product. The physical properties of many metals depend largely on the heat treatment they receive, and inasmuch as many pieces have had much labor expended upon them before heat treating, only the most dependable equipment should be used in order to avoid waste.

The electric furnace as a heat-treating tool of precision calibre has not only contributed to the elimination of waste resulting from improper heat treatment, but it has become a means whereby many of the high standards of modern industry are maintained. Much of the speed and safety of our present day civilization depends on our ability to reproduce accurately the ultimate physical properties obtainable in metals. Imagine, if you can, our giant aircraft thundering from New York to Los Angeles between breakfast and dinner, or the new streamlined trains hissing

Fig. 1.—Return Recuperative Pusher Type Furnace.



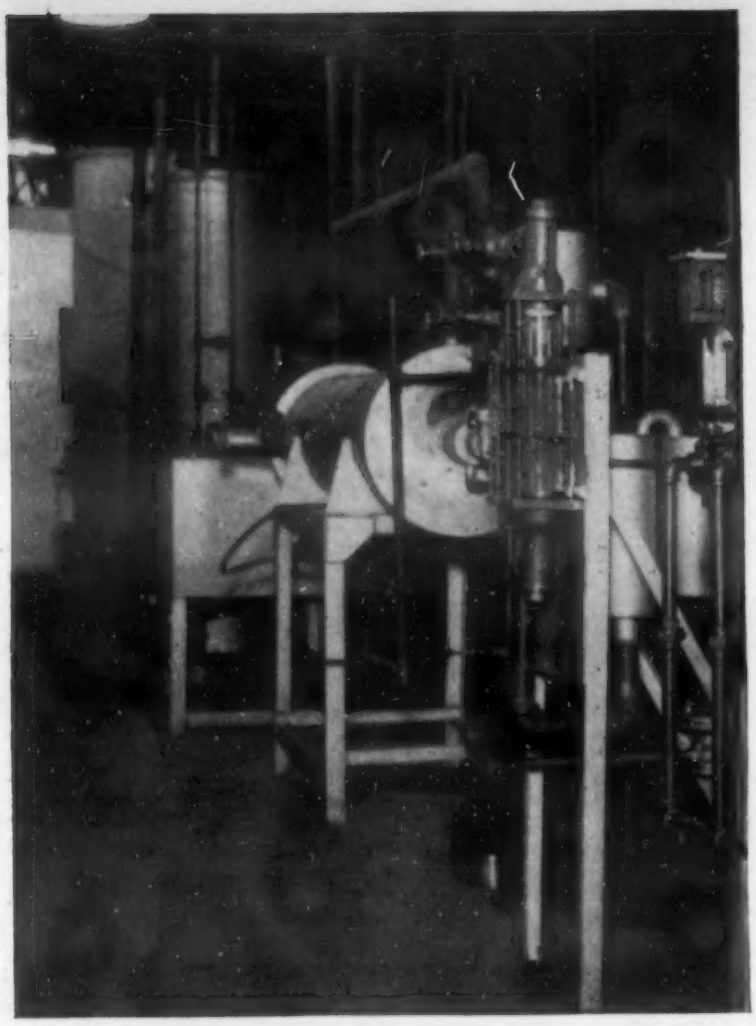


Fig. 2.—On Right of Furnace is the 300 cu. ft. per hr. Atmosphere Equipment.

across the plains at 100 or more miles per hr., if it were impossible to reproduce accurately the form and properties of each individual part.

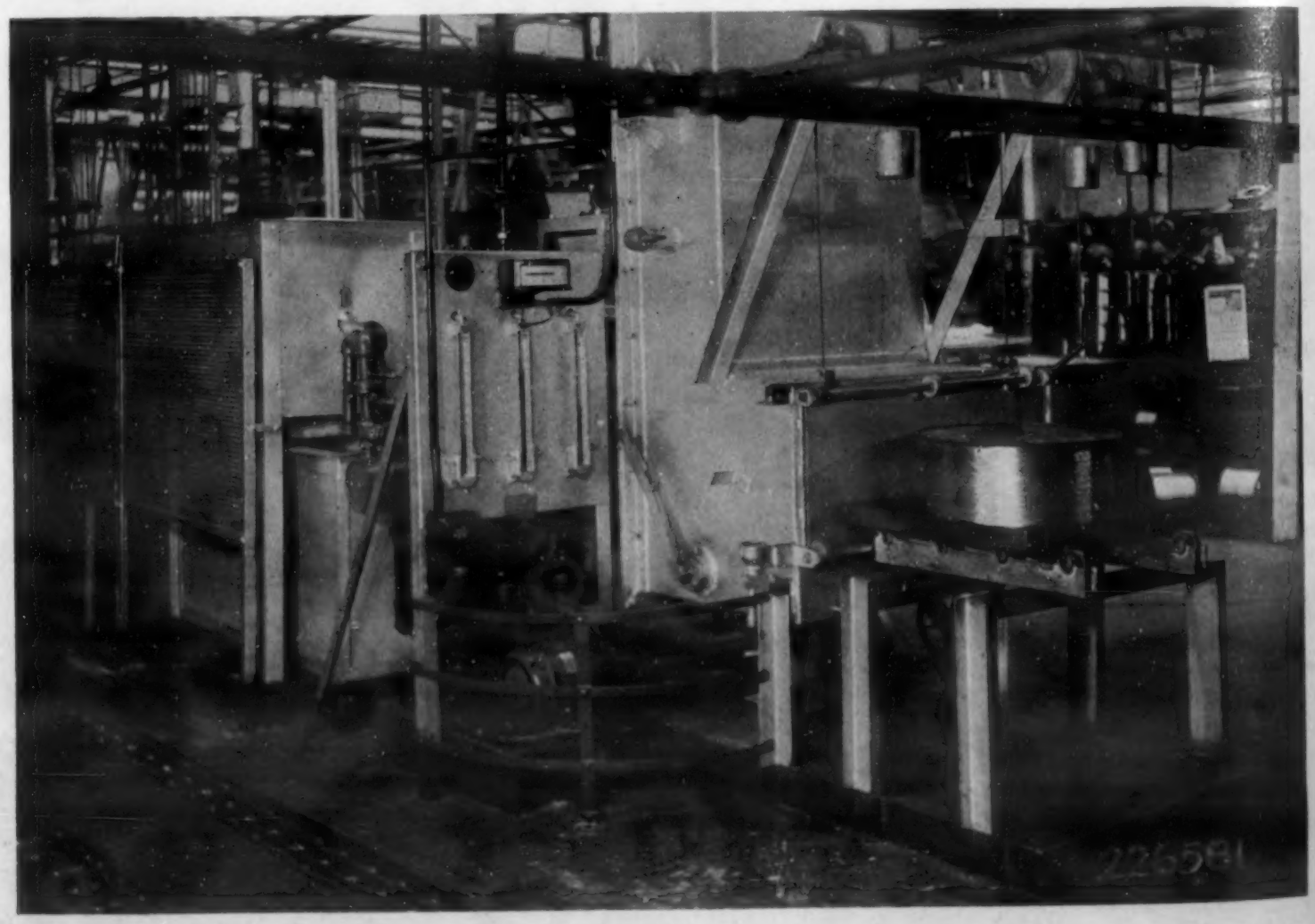
Many materials go to make up the modern transport plane, but let us consider only one of the metals—copper—which is used for tubing and wiring, and through which flows vital fuel and energy to the powerful motors. These copper parts must certainly be of highest quality to insure the safe comfortable travel to which we have become accustomed, and such high quality can only be obtained by uniform manufacture, including the accurate control of the many heat-treating processes to which the metal is subjected before it attains its final shape.

Some Facts About Copper

Copper, as one of our oldest metals, has been produced and heat treated in many ways. Some of the older methods of manufacture still persist but, fortunately, the process of annealing is undergoing a change which will result in a finer, more uniform material with which our engineers may work. During the last decade, the cost of electric energy has gradually decreased, and this fact, together with the introduction of inexpensive protective atmospheres, makes economically possible the use of electric furnaces for bright annealing copper and many other non-ferrous metals and alloys. Not only can the highest standards of uniformity be obtained, but with the aid of protective atmosphere, the electric furnace can be made to produce a clean, dry, bright product without the need for the expensive and time consuming cleaning and drying operations that are still used in the older methods of manufacture.

The scientific manner in which heat can be distributed throughout the electric furnace, together with the accurate temperature control obtainable, produces uniform heating that does much to eliminate the tendency of fine wire and thin sheet to "stick." Sticking or clinging of the metal to

Fig. 3.—Straight Through Pusher Furnace and Atmosphere Equipment Used for Bright Annealing Copper Wire Spools.



the spool or reel as it is being unwound produces, in the case of wire to be enameled, irregularities and kinks which cause a non-uniform coating of enamel, commonly referred to as being "beaded." Wire with such an inferior layer of enamel is useless, and represents much waste that might have been avoided if the metal had been given the proper heat treatment.

Electric furnaces for practically any heat-treating process may be designed embodying automatic handling of the charge with any one of several types of conveyors. The furnaces most widely adopted for bright annealing copper are the belt conveyor, pusher and bell types. The photographs illustrate more recent installations of pusher and bell furnaces with their protective atmosphere equipments, but before describing them, the method of manufacturing the atmosphere will be discussed. The production of the atmosphere is an important step in obtaining bright-annealed copper, and a working knowledge of its preparation is essential.

Production of the Atmosphere

In general, protective atmospheres are made by burning a fuel gas with an insufficient quantity of air and subsequently purifying the products of combustion to eliminate the deleterious components. A good atmosphere may be prepared from carburetted water gas, chosen here because its treatment will serve to illustrate the elimination of sulphur gases from the products, an additional problem not present in the preparation of an atmosphere from natural gas. A pump or an automatic mixing machine is used to mix intimately gas and air in just the right proportions and force them under 2 or 3 lbs. per sq. in. pressure into a refractory lined combustion chamber where they are allowed to burn in the presence of a catalyst and at a temperature in the neighborhood of 2000 deg. F.

In some cases where high pressure gas and air are available, the mixing pump may be replaced by two pressure regulators which reduce both gas and air to the same pressure of 2 or 3 lbs. per sq. in. The mixing then takes place either at the burner or in a pipe line just ahead of the combuster. The quantity of air used is just short of that required for perfect combustion, resulting in products that contain small amounts of such gases as CO, H_2S, H_2 and SO_2, besides CO_2, H_2O and N_2, the latter three gases forming about 85 per cent of the total volume. The burned gases are then led into the purifying system, where the first tower contains limestone over which water is allowed to trickle. As the gases pass through the limestone tower, the SO_2 formed during combustion is readily absorbed by the water along with small quantities of H_2S. Limestone makes the water slightly alkaline, in which condition it is believed to be more effective in removing the acid forming radical SO_2.

Next, a tower containing iron oxide heated to and maintained at about 100 deg. F. is used to remove the remaining H_2S. Then the water vapor resulting from the combustion of hydro-carbons or entrained during passage through the limestone tower is reduced to a sufficiently low concentration by passing the gases through a refrigerated compartment maintained at approximately 40 deg. F. It is important to remove the water to saturation as low as 40 deg. F to prevent condensation on the inner surfaces of the furnace cooling chamber, which would result in water spots on the bright surface of the copper being annealed. The remaining gases, mainly CO_2 and N_2, make up the inert atmosphere.

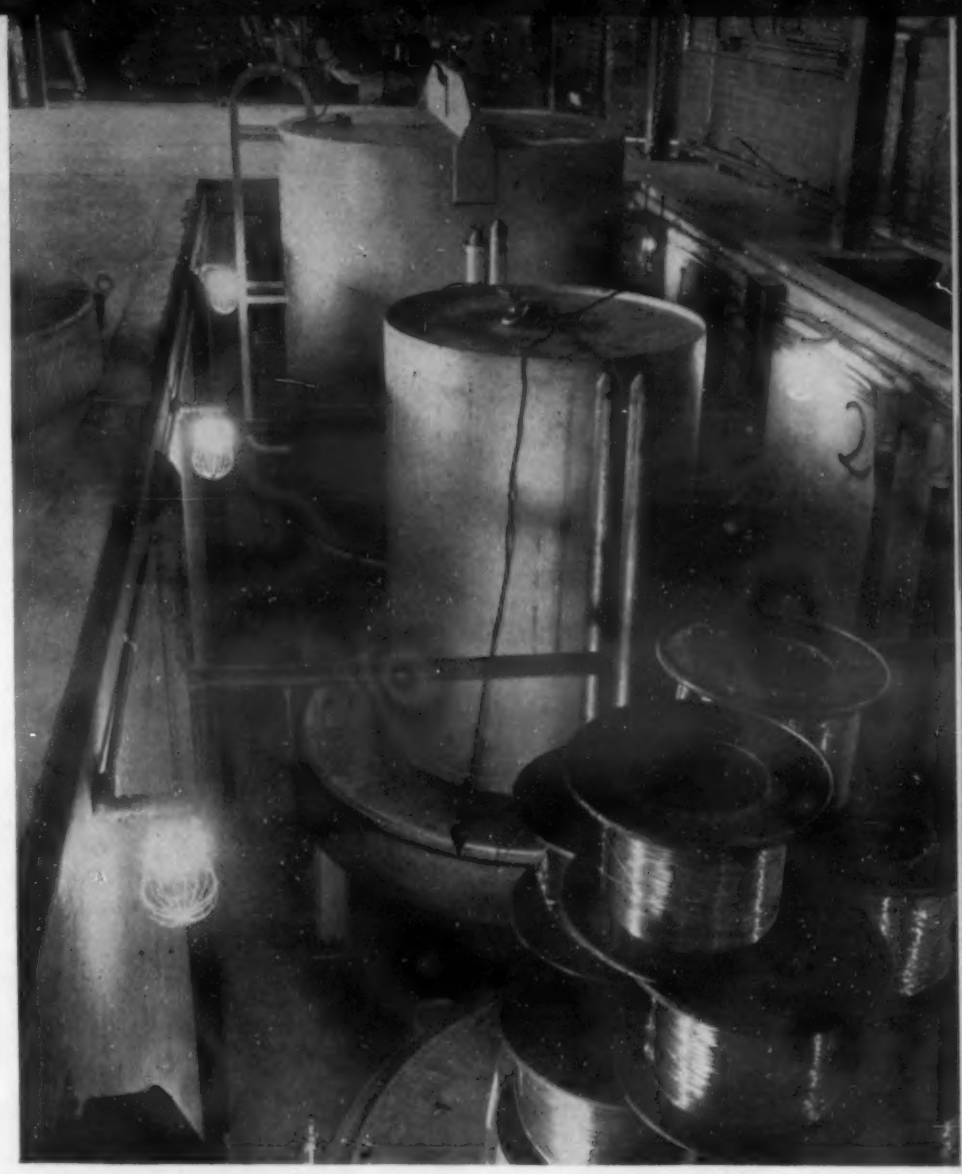
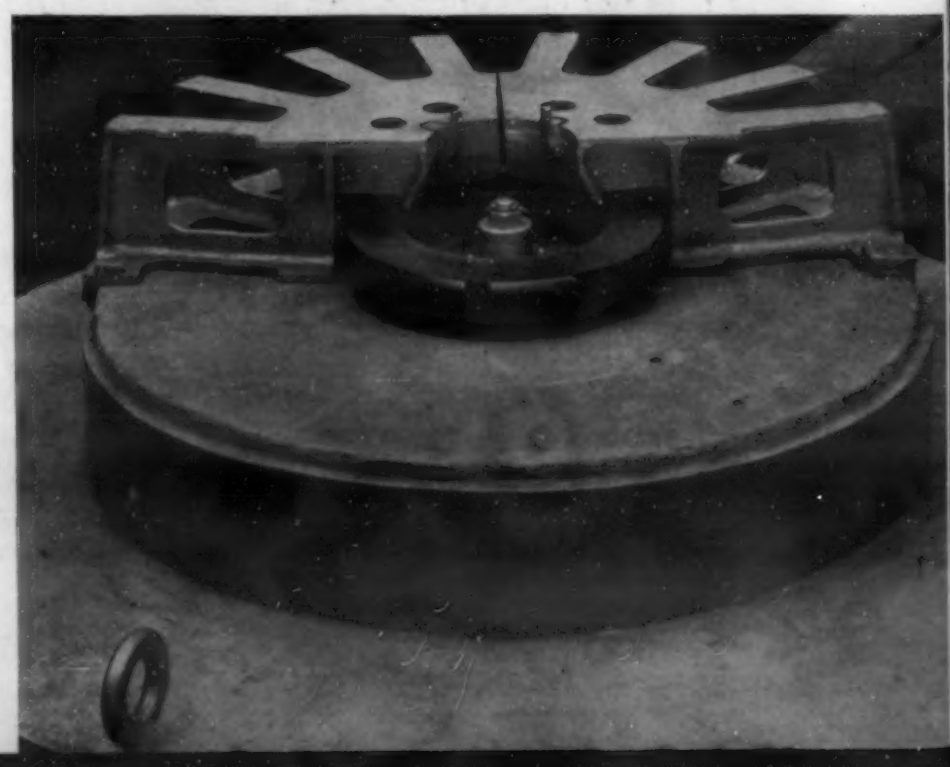


Fig. 4—Bell Furnace Installation.

The Air to Gas Ratio

One of the most essential requirements in operating an atmosphere equipment such as has just been described is to keep the air to gas ratio constant. If the ratio of air to gas becomes too low, considerable quantities of such reducing gases as H_2 and CO will be formed, and these gases, if present in too large amounts, may produce embrittlement of copper. In the case of fine copper wire or thin sheet and tubes, such embrittlement may be so pronounced as to render the product useless. Another danger of a low air to gas ratio is the formation of large amounts of H_2S, which is at best a difficult gas to eliminate from the products, and if present in large quantities, may pass on into the furnace, where it will produce a copper sulphide tarnish upon the surface of the hot copper.

Fig. 5.—Close-up of One of the Bases of the Bell Furnace Installation.



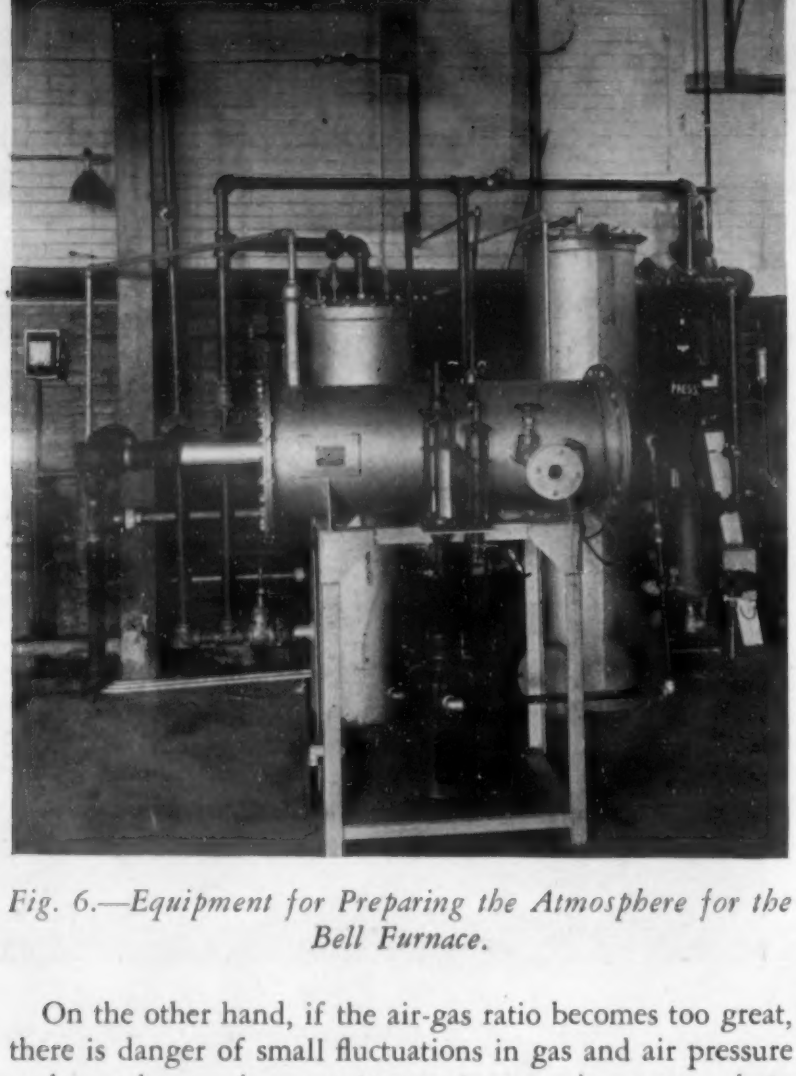


Fig. 6.—Equipment for Preparing the Atmosphere for the Bell Furnace.

On the other hand, if the air-gas ratio becomes too great, there is danger of small fluctuations in gas and air pressure or large changes in room temperature causing excess air to be drawn into the system. Since there is no provision in the purifying system for the elimination of oxygen, even a small quantity passing into the hot furnace would discolor the copper by forming copper oxide.

An analysis of the atmosphere just before it passes into the furnace may be made with an ordinary Orsat apparatus where the percentage of CO present serves as a check on the suitability of the atmosphere for use in bright annealing copper. The limits are from 1 to 2.5 per cent. More than 2.5 per cent CO represents too low an air to gas ratio, while less than 1 per cent means the ratio is too high, and unless the ratio is adjusted to constantly produce between 1 and 2.5 per cent CO, there is likely to be trouble from discoloration, or embrittlement.

Relieving "Strain Hardening"

In annealing copper to relieve "strain hardening" caused by rolling or drawing operations, it is necessary to allow recrystallization to take place at some temperature within the softening range, usually between 500 and 1200 deg. F. This process requires an integral of time and temperature depending upon the amount of cold working previously undergone by the metal, and for any given amount of cold work, the time necessary depends upon the temperature.

After the copper has been heated to the proper temperature, it must be cooled to about 150 deg. F. before it can be removed from the furnace, or it will be tarnished by oxygen in the air of the room. It is therefore necessary to provide cooling chambers in which the charge may cool while in the presence of the furnace atmosphere. For a continuous furnace, such a chamber may be simply water jacketed or may contain fans and cooling coils which cool and recirculate the atmosphere over the work. In this connection, it may be said that fans add greatly to the heat transfer between the copper and cooling water. As a matter of fact, their use in heating chambers proper is being widely adopted, because of the marked shortening of heating time effected.

The reason that fans are so important in bright annealing furnaces is that bright surfaces have a very low coefficient of emissivity—that is, poor ability to radiate or absorb heat— and unless additional heat is supplied or removed by forced convection, the heating and cooling time would be unnecessarily long. This means longer furnaces, requiring additional valuable floor space. It has been found that as much as 70 per cent of the heat required for annealing may be transferred by means of forced convection in the case of bright annealing copper.

Types of Furnaces

One type of furnace that takes advantage of fans is the return recuperative pusher type furnace shown in Fig. 1. Not only does this furnace employ fans for heat transfer, but it makes use of the cold ingoing material to cool the outgoing charge. The heat gained by the cold metal from the outgoing material is about 30 per cent of that required for annealing, which means a sizable saving in power consumed. The furnace shown was designed for copper strip ranging from 15/16 in. to 18 in. wide, with a minimum thickness of 0.004 in. The smallest coils weigh 30 lbs. each, while the larger ones weigh 150 lbs. The average production of the furnace is 2300 lbs. per hr. at 1200 deg. F.

The furnace consists essentially of a heating chamber shown at the left of the photograph, a recuperating zone in the center, a water jacketed cooling chamber, and a double flushing chamber at the right. The conveyor is made up of two lines of cast trays which are moved into and out of the furnace, one tray at a time, by means of hydraulic cylinders. The trays are supported on rollers so that they may be moved with the least possible effort. All operations, except placing the charge in the flushing chamber, are accomplished automatically by means of a timing device and solenoid operated valves in the hydraulic pusher system.

At the right of the furnace in Fig. 2 may be seen the 3000 cu. ft. per hr. atmosphere equipment which essentially consists of the apparatus described above. It is interesting to note that although the natural gas used in this installation was reported to be sulphur free, there were times when for no apparent reason the metal being annealed acquired a sulphide tarnish. It was necessary to install purifying equipment similar to that used for manufactured gas.

Fig. 3 shows a straight through pusher furnace and atmosphere equipment used for bright annealing copper wire on spools, each spool weighing 350 lbs. The furnace is rated at 1000 lbs. of copper per hr. at 1000 deg. F., while the gas equipment is capable of producing 1000 cu. ft. per hr. of conditioned atmosphere. Two duplicate installations by a large manufacturer, one in operation for two years, the other to be installed shortly, are used to anneal fine, hard drawn copper wire in sizes down to 0.003 in. diameter.

A bell furnace installation and a close-up of one of the bases are shown in Figs. 4 and 5. The product, as can be seen, is wire and ranges from 0.036 to 0.010 in. diameter

wound on reels. In the center of the photograph is shown the hood or metal cover that is placed over the charge just before heating and which remains there while the charge is heated and cooled. The hood, which is sealed in a water trough at the bottom, furnishes a compartment for the charge in which a protective atmosphere can be maintained. As soon as the hooded charge has been heated for a sufficient time, the bell or furnace, shown at the left, is removed and placed over another charge. The previous charge is cooled by means of water being sprayed over the hood. The fan, mounted in the base, circulates the atmosphere under the hood through the copper coils, during the entire heating and cooling cycle.

Preparing Atmosphere for Bell Furnace

Atmosphere for the above bell furnace is prepared in the equipment shown in Fig. 6. The combuster is shown in front with the purifying towers in the background. The two instruments mounted on the front of the combuster indicate the relative amounts of gas and air being pumped to the combustion chamber by the automatic pump mounted below. The combuster is provided with a fire check to prevent backfiring and a lighting hole placed conveniently near the burner end. A small torch using gas from the mixture line is used to light the combuster through the lighting hole. This method of ignition makes it possible to start the apparatus immediately and have conditioned atmosphere available within ½ hr.

An older method of lighting in which the combuster was filled with raw gas and lighted at the exit end before admitting air until the flame became short enough to be drawn inside, would invariably cause delay. Often, as the flame would be drawn back into the combuster, the sudden ignition of the chamber full of combustible mixture would cause a report not unlike that of a fair-sized field piece, and instead of continuing to burn, the flame would go out, making it necessary to repeat the process. However, with the numerous installations of controlled-atmosphere electric furnace combinations, the many early problems in operating technique have been solved.

Some Results

In each of the above installations the annealed metal is taken directly from the furnace and either reduced further or sent directly to the user. No longer is there need for costly cleaning or drying operations after annealing, and even though copper does not require as close temperature control for annealing as do some of the ferrous metals, it has been found that the electric furnace definitely insures to the user a consistently uniform and high grade product.

The foregoing has dealt with the furnace technique. Metallurgically, the necessity for and the suitability of such treatment is more understandable nowadays than in earlier times.—Editor.

Supplementary Comment

By P. H. BRACE, Consulting Metallurgist Westinghouse Electric & Mfg. Co.

"COPPER IS COPPER," said the old-timer in the frame of mind of Gelett Burgess' station master who maintained that "pigs is pigs." Present-day refinements in construction and manufacture have brought about recognition of several varieties of copper and have also made it necessary to carefully adjust heat treatment and mechnical processsing to avoid irregularities of strength, ductility and other properties which would have gone unnoticed in the days when copper was considered to be annealed if it had been heated red hot and thrown into a tank of water.

Times have changed. "Mysterious" failures first led to studies of the effect of reducing atmospheres on copper. The work of Pilling showed that the commercial "pure" copper contained certain amounts of oxygen in the form of minute particles of cuprous oxide, Cu_2O, disseminated throughout its mass. It was found that the embrittlement which occurred when copper was heated in atmospheres

Fig. 1.—Annealing Curves for Cold Rolled Commercial Copper at 300 deg. C.

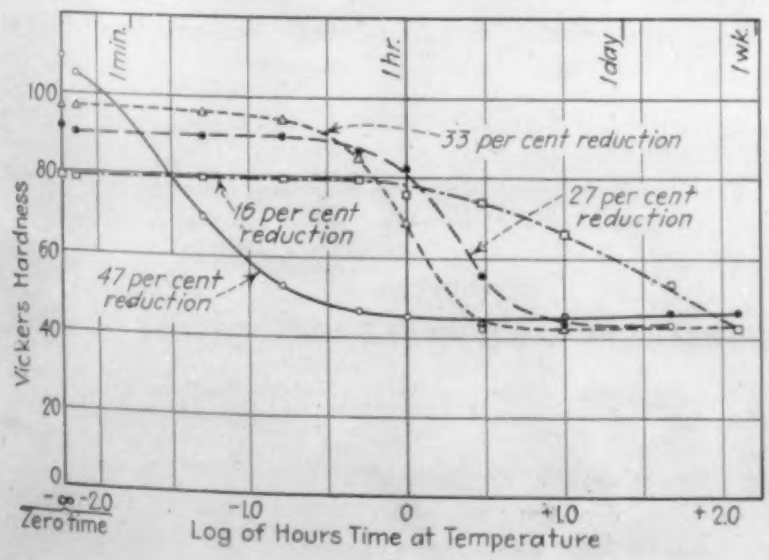
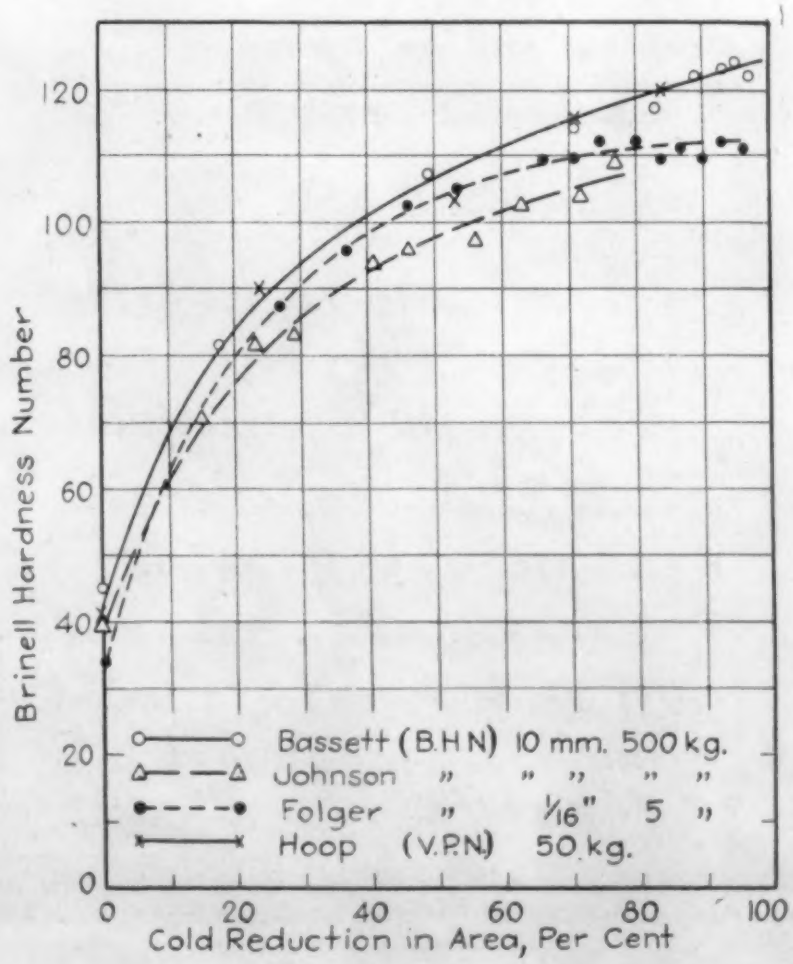


Fig. 2.—Effect of Cold Rolling on Hardness of Copper.



containing hydrocarbons, carbon monoxide and in particular, hydrogen, was due to the gaseous products formed when hydrogen, for example, diffused into the copper and reacted with the cuprous oxide as follows:

$$H_2 + Cu_2O = H_2O + 2Cu$$

Hydrogen diffuses readily through hot copper, the water with difficulty. As a result of this "one-way traffic", high steam pressures develop in the neighborhood of the copper oxide particles forcing apart the crystals of the copper and forming fissures which in extreme cases reduce the ductility of the copper to approximately that of chalk.

Embrittlement is favored by high annealing temperatures, high concentration of reducing gases such as H_2, CO and hydrocarbons, and by prolonged heating in such atmospheres. Experience has shown that for temperatures below 400 deg. C. and concentrations of H_2 and CO below approximately 1 and 2 per cent respectively, even fine wire may be annealed without showing noticeable embrittlement. The approximate time-temperature curve is shown by Fig. 1.

The response of copper to annealing is greatly dependent upon its previous mechanical history. When the metal has been severely deformed, it "anneals" most rapidly and completely. The effects of deformations of a few per cent may be quite difficult to erase. The effects of cold work on the annealing characteristics of a typical specimen of commercial copper such as that commonly used for electrical conductors are illustrated by research curves, Nos. 204,966 and 198,670. It will be noted that the curves for severely cold-worked copper actually cross those corresponding to small reductions. Low annealing temperatures are also desirable from the standpoint of grain-size and ductility.

Silver in Copper

In general, the more nearly pure a metal is, the lower is its annealing temperature and copper is no exception to the rule. Quite small amounts of alloyed metal profoundly influence its response to heat treatment after mechanical working of which silver is an outstanding example. It is interesting to note that although the silver confers upon the copper a marked increase in "thermal endurance", it has a relatively small effect on its physical properties and response to cold work. The physical properties of the cold-worked silver-bearing copper differ but slightly from those of pure copper similarly treated.

Because of its high thermal endurance, silver-bearing copper is frequently used for making articles which must be subjected to heat in fabrication and use. Its peculiarities must also be taken into account in developing procedures for annealing it.

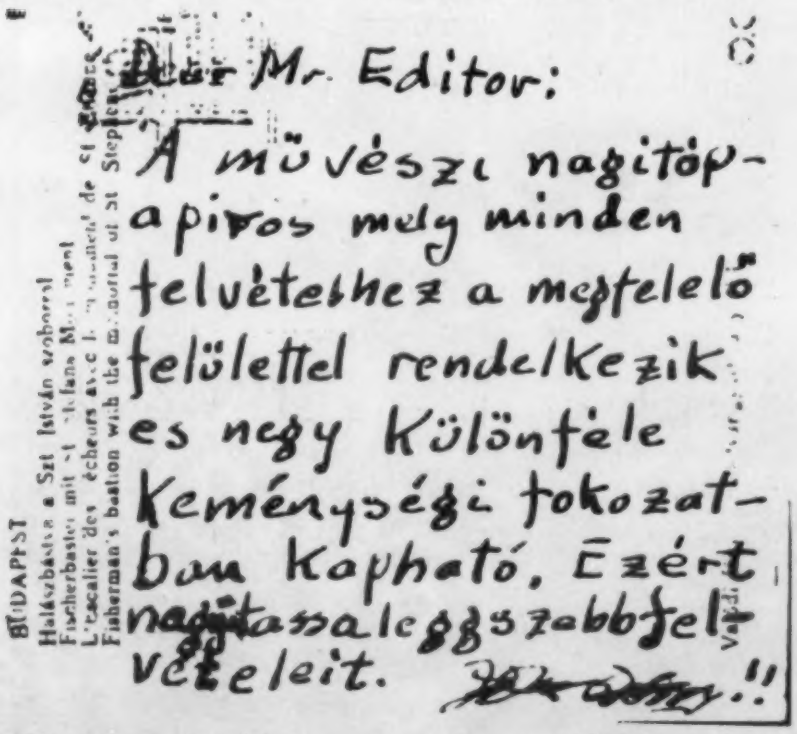
Recently copper nearly free of oxygen has been placed on the market. This material is characterized by exceptional ductility and substantial immunity to embrittlement by hydrogen. However, it is susceptible to oxygen and, if best results are to be secured, must be annealed in an oxygen-free atmosphere. In this case, the oxygen appears in "solid solution" and may cause abnormal grain growth and consequent irregularities in physical properties which are extremely undesirable in the difficult situations in which this specialized material is usually applied.

The foregoing will make evident the fact that the annealing of copper to meet modern industrial requirements is not a simple matter of "heat and dunk", but one requiring carefully developed procedures and well-designed and adequately controlled equipment in which to carry them out. In this field electric heat under automatic electrical control, in conjunction with proper furnace atmospheres, enables the production of metal combining flawless finish and uniform physical properties.

A Few Chuckles

A Problem and an Award

The communication, reproduced below, was received by our editorial director, postmarked from Berlin, Germany.



We fear he is calling us a son of a something, but offer a year's subscription for the first translation, including signature.—Editors.

Steel "Magnets"!

Headline, Columbus *Despatch Sun*, May 23.—"Steel Magnet to get honorary degree." The magnet turns out to be Mr. Fairless. —H.W.G.

Metals in the Hindenburg

From a Berlin dispatch to New York newspaper, commenting on the Hindenburg disaster:

> One of the first things brought to light about this big airship was that she had been constructed partly from the twisted framework of the British dirigible R-101 which crashed in France about six years ago. The *scrap iron* was purchased and shipped to Germany. (Italics ours.)

Can it be that British aluminum and American scrap iron entered into the construction of the Hindenburg!?!—E.F.C.

Platinum and Gold

"At the business end is ——'s renowned Scratchproof Point of Platinum and Solid Gold—the most inspiring and versatile point we have ever created. A point now having 33⅓% more gold than formerly, yet at no higher price to you."

Question, does the man in the street know that Pt costs more than Au, or doesn't he?

Crystalline Manganese Sulphide

IN CHILLED CAST IRON

by Owen W. Ellis

Director, Dept. of Engineering and Metallurgy, Ontario Research Foundation, Toronto, Canada

THE OCCURRENCE OF crystalline manganese sulphide in gray iron has been referred to by Allen[1], who in three excellent photomicrographs has demonstrated the habit of this material.

Crystals of manganese sulphide were apparently first noted by Levy[2] in some of the alloys investigated by him when studying manganese sulphides and silicates in iron and steel. Among other things, he shows in Fig. 8 of his paper, a trapezoidal section of a manganese sulphide crystal in Staffordshire cold-blast phosphoric iron. This crystal has much the appearance of some of those referred to in the discussion which follows.

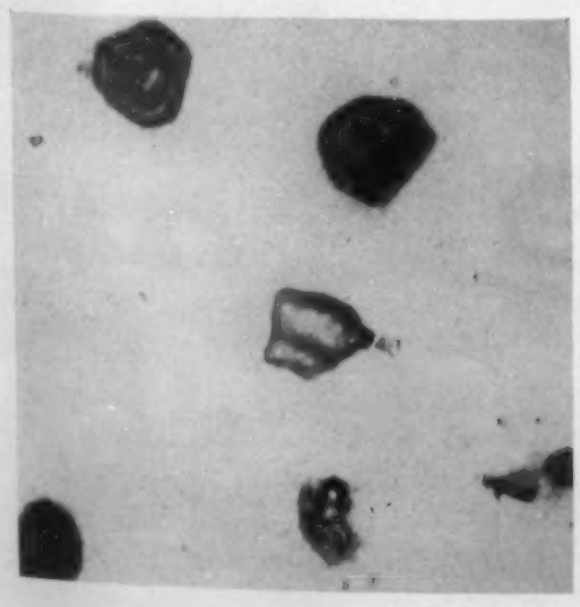
It does not appear that Wohrman[3] observed crystals of manganese sulphide in any of the materials used by him in the course of his investigations on inclusions. He states that pure manganese sulphide inclusions exhibit ordinarily distinct skeleton crystal outlines, and that solid solutions, rich in manganese sulphide, appear in cast metals in the form of very fine globules. However, he does not show photomicrographs of crystalline manganese sulphide of the type referred to by Allen, by Levy, and by the author in the present note.

Benedicks and Löfquist, in their book,[4] describe the morphology of manganese sulphide in the following terms, their remarks are quoted in full, even though some of them are not entirely relevant:

> "*β. Manganese Sulphide, MnS (with varying percentages of FeS:* In steel as rounded or crystallized grains—diameter about 2-10 μ. Colour dove-grey, lighter with increasing FeS-content. Generally occurring as isolated grains in the grain boundaries of the steel, but sometimes also in the austenite grains (Fig. 24, p. 41). More or less elongated with unbroken outlines, according to the deformation of the material (Fig. 27, p. 43). Sometimes associated with oxide (silicate) (Fig. 92, p. 116).
>
> "In pig-iron as typical dendrites as well as in the shape of rounded grains—diameter about 2-10 μ. The same colour as in steel. The dendrites occur independently of the grain boundaries, and consequently are often encountered in pearlite (Fig. 28, p. 43). See also *Wüst* and *Laval*, photomicrographs 1 and 2, p. 478."

The occurrence of crystalline manganese sulphide in chilled iron, so far as the author knows, is unrecorded in the literature. It was felt that a brief note on the subject might be of interest.

The appearance of such crystals in an unetched sample of chilled iron at a point approximately 1 centimetre in from the chilled edge of the block examined is shown in Fig. 1(a) at a magnification of 750 dia. Here can be seen



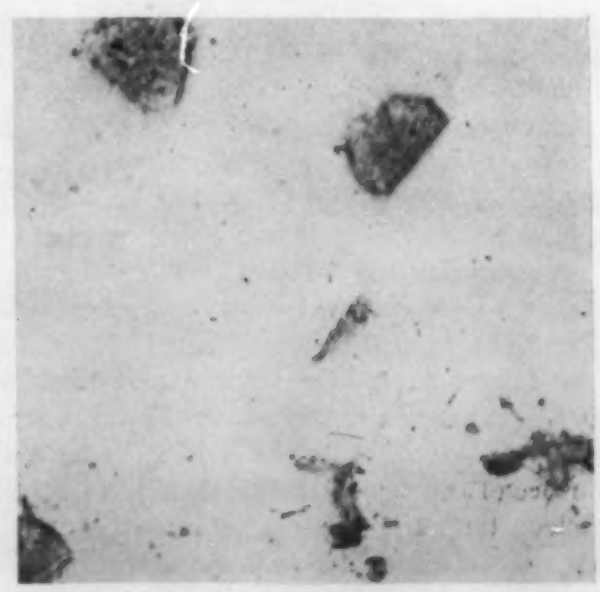


Fig. 1 (a) left and (b) right —Photomicrographs Illustrating Effects on Crystals of Manganese Sulphide of Immersing a Polished Sample in 10 per cent Chromic Acid Solution for 5 Mins. Magnification 750X. Fig. 1(a) is unetched.

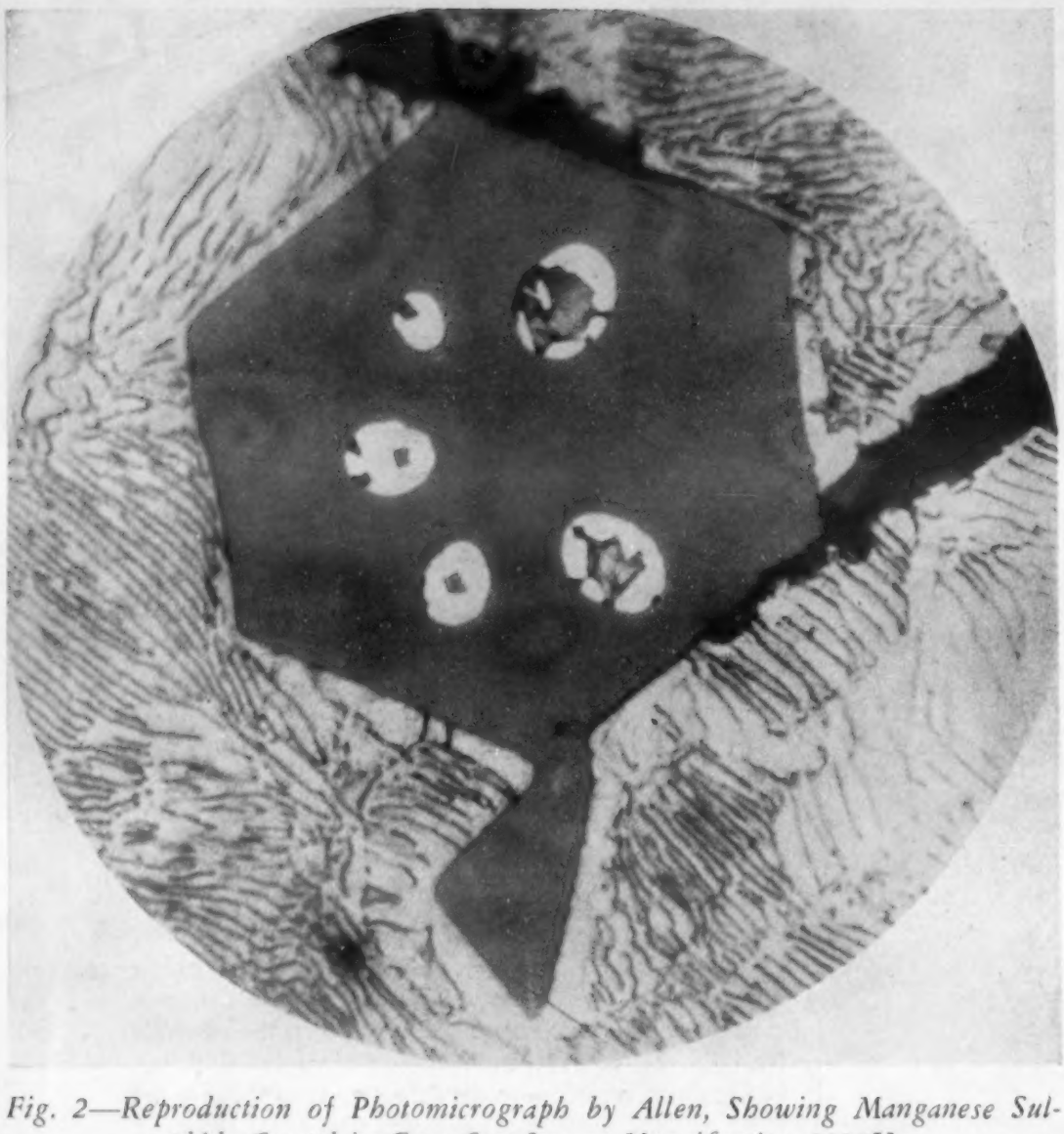


Fig. 2—Reproduction of Photomicrograph by Allen, Showing Manganese Sulphide Crystal in Gray Cast Iron. Magnification 3000X.

sections of six more or less perfect crystals of the compound (MnS).*

Note: For convenience we refer to the compound as manganese sulphide and give it the formula MnS, knowing, however, that such crystals may not be pure manganese sulphide, but rather mixtures of sulphides.

The author, not having read Allen's paper, at first thought these crystals to be graphite, which in nature occasionally occurs in six-sided tabular forms, having indistinct faces. The color of the crystals seen in cast iron is not far different from that of graphite, as may be observed if comparison be made between the color of the manganese sulphide crystal shown in Fig. 29 of Allen's paper (here reproduced as Fig. 2) and that of the small particle of graphite which still remains embedded in the trough that touches the crystal on its right-hand side. This similarity in color is not so clearly seen at low powers as at higher.

The effect of etching for 5 mins. in a 10 per cent chromic acid solution the sample of which Fig 1 (a) is a photomicrograph is shown in Fig. 1 (b). The sulphide has been completely removed as a result of this treatment.

Boiling, alkaline sodium picrate solution (Kourbatoff's reagent) is generally similar to chromic acid in its effect upon manganese sulphide. Fig. 3 (750x) shows an area in a sample treated for 1½ mins. in Kourbatoff's reagent. Here sections of two crystals can be dimly seen. These, because of their attack by the reagent, lie somewhat below the surface of the sample and hence are in poor focus. Nevertheless, the almost perfect square form of the one crystal and the trapezoidal shape of the other can be distinguished.

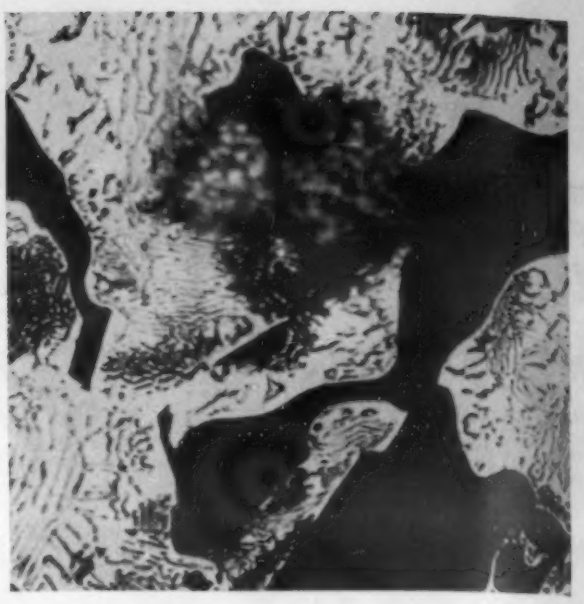


Fig. 3—Photomicrograph Showing Crystals of Manganese Sulphide Which Have Been Partially Dissolved in Boiling Sodium Picrate Solution, and which on This Account Lie Slightly Below the Surface of the Sample. Magnification 750X.

Fig. 4—Photomicrograph Showing Section of Manganese Sulphide Crystal Similar in Form to That Described by Allen. Magnification 750X.

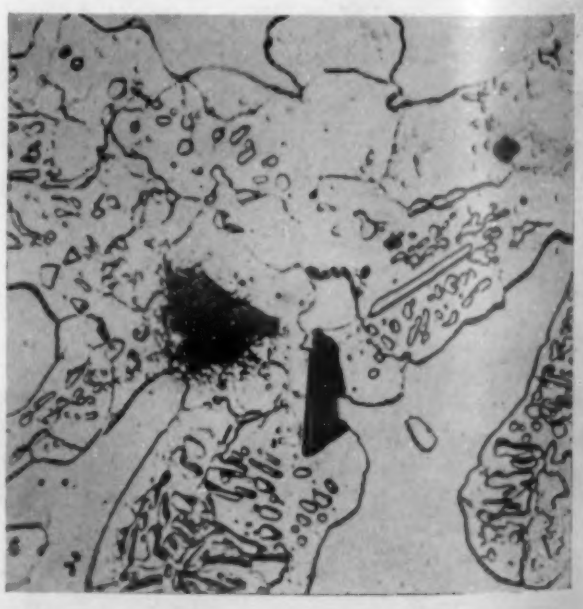


Fig. 5—Photomicrograph Showing Sections Through Two Manganese Sulphide Crystals. Magnification 750X.

Photomicrographs of sections showing other crystals are reproduced in Figs. 4 and 5. In Fig. 4, which is a photomicrograph at a magnification of 750 diameters of an area 0.365 in. in from the chilled face of a sample which had been annealed for some time at a temperature just below the critical, is shown a small, perfectly formed crystal of manganese sulphide, similar in appearance to that of Allen (shown in Fig. 2).

In Fig. 5, which is a photomicrograph (750x) of an area not far removed from that shown in Fig. 4, are shown sections through two other manganese sulphide crystals, these lying at such angles as to disclose areas triangular and quadrilateral in shape. Both crystals in Fig. 5 are embedded in primaustenoid ferrite.

These manganese sulphide crystals are distributed at random throughout the structure of chilled iron.

The question arises: Why should the sulphide inclusions most often found in cast iron differ in form from those most often found in cast steel? The real problem here is to explain why sulphide inclusions are sometimes crystalline and sometimes spheroidal in shape.

Let us admit that some sulphide inclusions do not freeze until after the steel in which they are found has solidified. Should one expect these inclusions when solid to be spherical, merely because they remained liquid after the steel had set?

It seems to the author that when sulphide inclusions remain liquid after the steel has set, their final form would be determined by the growing limbs, branches, and twigs of the dendrites in which they were enmeshed. Liquid inclusions would offer little or no more resistance to the pushes and pulls of the dendrites, plastic though the latter might be, than would the mother liquor from which the dendrites were crystallizing. Hence, in the solid steel the inclusions would exhibit the irregular outlines which occasionally characterize sulphide inclusions.

It seems probable that some sulphides which solidify in the melt at temperatures above the liquidus of steel acquire a crystalline outline while others acquire a spherical shape. In the former case the interfacial tension of the sulphide is greater in its effect than are the forces of crystallization; in the latter it is less. Spherical sulphide particles, once formed in the liquid steel, if sufficiently rigid at lower temperatures to withstand without deformation the pushes and pulls of the growing dendrites, will appear in the solid steel as spheres, while crystalline sulphide particles, once formed in the liquid steel, given the same general properties, will appear as crystalline inclusions in the solid steel.

It does not seem altogether impossible that crystalline sulphide particles formed in solid steel, could as a result of a change in the interfacial tension, transform into spherical inclusions in the solid steel.

Speaking generally, however it would appear that the tendency for sulphides, whatever their composition, to form crystals rather than spheres in liquid steel or cast iron increases as the temperature of the melt is lowered, so that sulphides which in steel are trapped as spheres in cast iron are found as crystals. The point that the author would like to emphasize is that, because an inclusion is spherical in shape, it does not of necessity mean that it remained liquid below the solidus of the alloy in which it is found.

That the sulphides in steel may be generally different from the sulphides in cast iron may, of course, account for the usual differences between the shapes of the inclusions in these materials. It seems more likely, however, that physical, rather than chemical, influences are the more important in the connection.

Note: Native manganese sulphide (Mns)—Alabandite—is isometric-tetrahedral; usually granular massive. Cleavage: cubic, perfect (Dana, "Text Book on Mineralogy").

References

[1] *Transactions*, American Foundrymen's Association, Vol. 39, 1931, pages 785-787.

[2] *Carnegie Scholarship Memoirs*, Iron and Steel Institute, Vol. 3, 1911, pages 260-319.

[3] "Inclusions in Iron." *Transactions*, American Society for Steel Treating, 1928. (Reprint).

[4] Benedicks and Löfquist. "Non-Metallic Inclusions in Iron and Steel." Chapman and Hall, London, 1930, page 176.

Major Robert A. Bull

1874-1937

Death came to Robert A. Bull unexpectedly on Wednesday night, July 28, 1937, at the home of a friend and client, Mr. O. M. Kilby, President of the Kilby Car and Foundry Co., in Anniston, Alabama. He died in his sleep, the victim of heart failure.

The news of "Bob's" passing comes as a tremendous shock to his countless friends, endeared to him by his unusual warmth of feeling and capacity for friendship. My own sense of grief at his passing is especially profound, as it has been my very good fortune and great pleasure to have shared his friendship for twenty-five years.

At the time of his death Major Bull maintained a widespread consulting practice, particularly to the steel foundry industry, of which he has justly been called the outstanding authority. The success of his practice was merited not only by his wide practical experience in the foundry industry, but by his education as a metallurgical engineer. Coupled with these was his unusually sound judgment, based on a constant, insistent demand for the facts concerning every situation.

He was born at New Albany, Indiana, June 28, 1874, received his B. A. degree from Butler College in 1897 and his M. A. from St. Louis University in 1914. From 1893 to 1920 he was associated successively with Robert W. Hunt and Co., various steel foundries and the U. S. Army Ordnance Dept., A. E. F.; he was commissioned Major in the Ordnance Reserve Corps. From 1920 to 1934 he was Director of the Electric Steel Founders Research Group. He has been a frequent contributor to metallurgical literature, with a long list of published material.

Major Bull was a member of every important metallurgical or foundry society in this country and two in Britain, and of other scientific or government-service associations. In the work of the Amer. Foundrymen's Assoc., the Amer. Soc. for Testing Materials, the Amer. Soc. for Metals and the Steel Founders Soc. of America he has for many years taken an active part, with a long list of committee assignments, to which he devoted a tremendous amount of time, energy and sincere effort. At annual conventions his schedule of meetings was so crowded that he seldom enjoyed the usual relaxations offered by such occasions, although he never lost an opportunity for a friendly chat with his friends in the corridors, at meals or after his long day's work was done.

His efforts in behalf of the Amer. Foundrymen's Assoc. were unusually valuable and he was elected to its presidency in 1915 and 1916; probably his most significant accomplishment since was the organization and leadership of the National Research Council Committee on Molding Sand, organized in 1921. In 1927 he was awarded the Joseph S. Seaman medal for his unremitting and conscientious work in connection with the affairs of the Association and for his standing and accomplishments in the foundry industry.

No person could have been held in higher esteem by his friends. And just as one always felt better for having been in his company, so has he permanently and immeasurably enriched the great industry he served so well.—*G. H. Clamer.*

Bob Bull completed over 40 years of service to the steel castings industry and died in harness, as he would have preferred.

He felt that a technician must give as well as take, and in discussions at meetings, in private talks, and by correspondence, he was always helpful. His work on the Editorial Advisory Board of METALS AND ALLOYS was an example of the unselfish interest he took in everything tending to advance foundry metallurgy and foundry practice.

Although his war service with Ordnance gave him the title of Major, he was "Bob" to his friends, and his friends were all who had contact with him. A positive personality, always standing up for the right—no one was ever in doubt as to Bob's convictions—his sincerity brought respect and love from all his associates. Moreover, to Bob a man was never just John Jones of the A. B. C. Company; he was interested in John Jones as a person. He liked people, and liked to help them. His Christmas cards were interesting little essays, expressing his own personality.

One's first thought on hearing of his death is a personal one, the loss of a dear friend; the second, that the foundry industry has lost a technical leader, one whose influence will live long.—*H. W. Gillett.*

NOTES ON THE GRAIN SIZE OF

Cast Ni-Cr Heat-Resisting Alloys

by F. K. Ziegler and L. B. Haughwout

Metallurgical Engineer and Radiographer, Respectively, The Electro-Alloys Co., Chicago

INVESTIGATIONS OF THE MICROSTRUCTURE of the high nickel-chromium alloys have been undertaken for several years, chiefly by the manufacturers and by laboratories such as that maintained by the Union Carbide & Carbon Corp. The small amount of published information on the microstructure of these alloys is probably a result of a lack of widespread interest in their fundamental properties. While much of the information obtained upon the behavior of these alloys under various service conditions has been correlated with the carbide formations, little study has been made of grain size. Since recent advances in furnace construction have made advisable a closer study of the physical properties, more accurate metallographic information is required.

There is little difficulty in showing the grain boundaries in the low carbon rolled alloys of the nickel-chromium series, (35% — 65% Ni; 15% — 20% Cr), but where large quantities of the carbide constituent are present, as in the commercial alloys used for castings, (0.40% — 0.75%), attempts to show grain boundaries are often confused with the carbide formations which are clearly brought out. Because existing microscopic methods failed in so many instances to give reliable information on grain size, and because the apparent grain size indicated by the photomicrographs was not always consistent with existing theories, the authors applied methods of X-ray diffraction analysis in an effort to obtain more accurate information. In making these studies, some apparent anomalies were discovered which resulted in the formation of new ideas on the microstructure of these alloys. Collaboration by the Union Carbide & Carbon Research Laboratories with the authors resulted in the verification of these ideas and the development of suitable metallographic methods of grain size determinations.

Two Distinct Types Involved

We may divide the microstructure of the cast alloys into two distinct types according to their appearance. There are, of course, various intermediate structures. The first type which is typical of most of the alloys in the as-cast condition is that in which the carbides are arranged in a more or less regular fashion having the general appearance of a network, Fig. 1. In this type of structure, it has been generally assumed that the grain boundaries followed the lines or stringers of carbides which make up the network.

The second type of structure is that in which the carbides are arranged at random with little or no evidence of a network. This type of structure is typical of the alloys after they have been subjected to high temperatures for long periods of time in commercial service. It is occasionally found in certain types of castings in the as-cast condition. In this type of material, the common etching reagents used to bring out the carbide structures reveal little if any reliable evidence of grain boundaries.

It seems logical to assume that the easy exposure of the carbide particles is due to the ready attack of the etching reagent at their boundaries, which, if we accept the chromium impoverishment theory of Bain, are lower in chromium than the balance of the grain. By the time that the actual grain

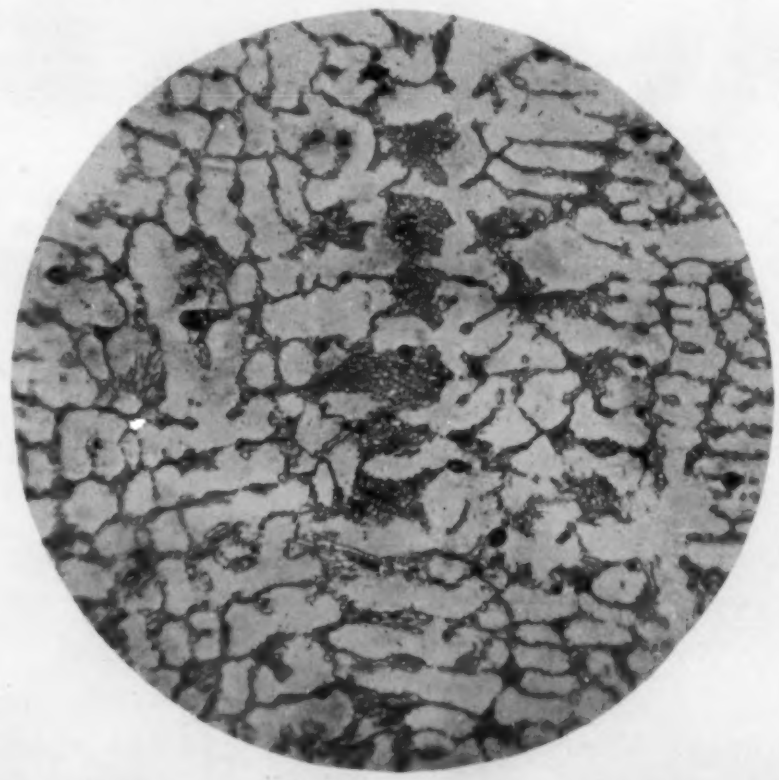


Fig. 1.—Carbides Arranged in a More or Less Regular Fashion Having the General Appearance of a Network. Magnification 100X.

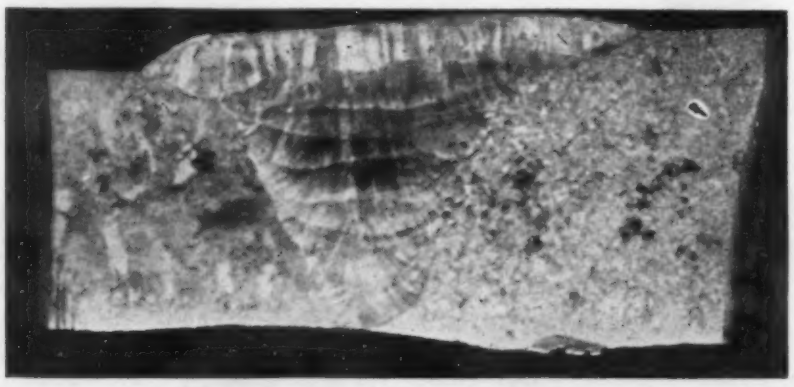
boundaries are attacked, the specimen is so stained by the end products of the etching reaction that it is impossible to get an idea of the true structure. In view of these facts, methods of X-ray diffraction analysis were applied to the problem of determining the grain size of these alloys.

In making the Laue photographs, the unfiltered radiation from the tungsten target of the X-ray tube employed in the routine radiographic inspection of castings was used. The tube was operated at 200 Kv. and 5 milliamperes. The aperture nearest the tube was 0.070 in. in diameter. The second aperture was 0.035 in. in diameter and was separated from the first by a distance of 4 in. A small lead absorber was placed over the center of the film holder to prevent undue scattering by the primary beam.

The specimens were cut out with a hacksaw, ground to a thickness of 0.125 in. and etched to a final thickness of 0.075 in. It was found that this thickness gave a more representative pattern and was easier to prepare than the thinner specimens usually employed in this kind of work. The time of exposure was only 15 mins. Several hundred patterns were made in the course of this investigation.

Several Interesting Facts

Preliminary X-ray diffraction studies on alloys having well defined carbide networks disclosed several interesting facts.



PART A PART B

Fig. 2.—A Piece of High Carbon 65 Ni-15 Cr Alloy Which Had Not Been In Service (Part A) Welded to a Piece of Similar Alloy (Part B) That Had Been in Commercial Service Several Thousand Hours. A is as-cast and B is removed from service. Magnification 1.5X.

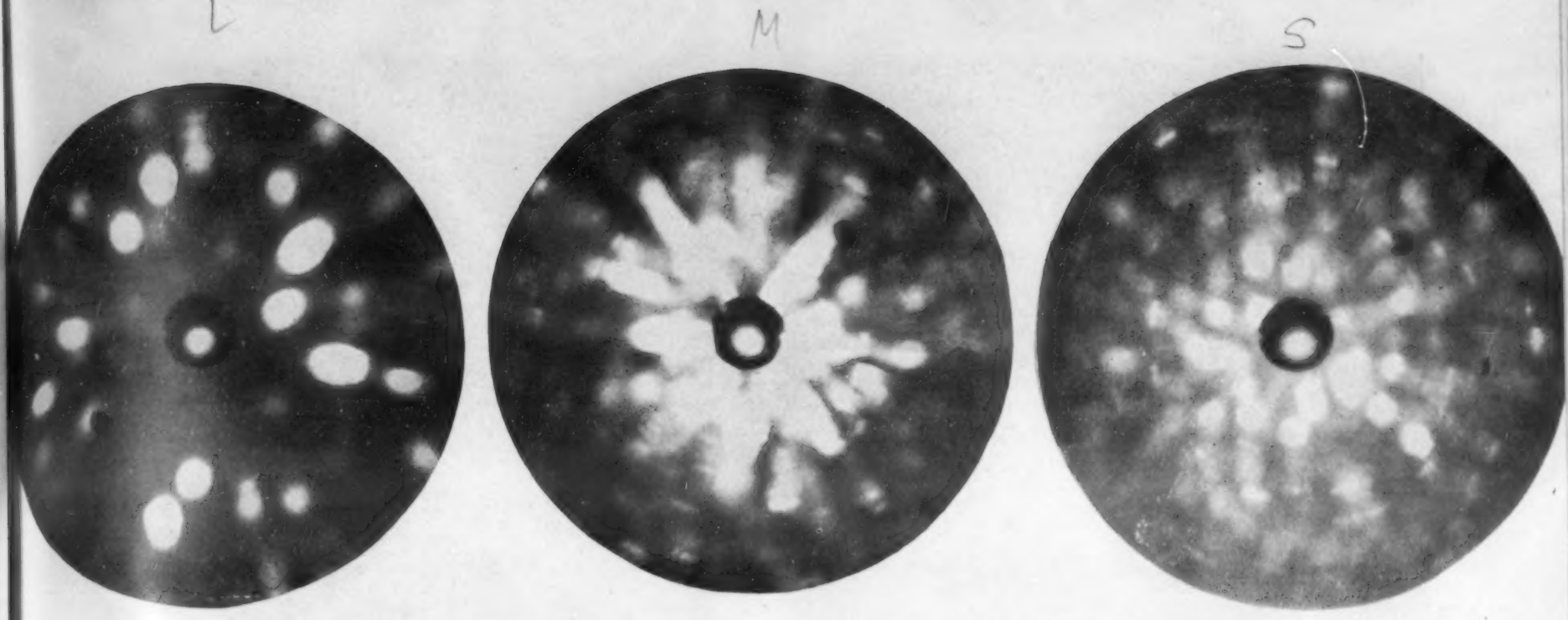
First: For a given alloy, no consistent correlation could be found between the micrographs and the diffraction patterns.

Second: The grain size as shown by the diffraction pattern was very much larger than that indicated by the carbide network. While it was reasonable to expect that patterns made on these alloys would be slightly different from those made on steel, the results were so vastly different that any explanation based on a difference in material or crystal structure was not reasonable.

Third: In spite of the above mentioned inconsistencies with the existing theories, there was one point worthy of note. Diffraction patterns made on thin cast sections showed a finer grain than patterns made on thick sections, provided both were cast under the same foundry conditions. A natural assumption is that the thin sections are of finer grain size than the thicker ones because of the chilling action of the mold.

The disparity that existed between the microscopic and diffraction methods is best illustrated by the following case which is taken from an investigation on the properties of the alloys which affect their weldability. (See "Welding of High Nickel Chromium Alloys," *Metal Progress*, October, 1936). Fig. 2 is a photograph (about 1.5X) show-

Figs. 3, 4 & 5.—Photomicrographs of the As-Cast Material (Top), the Weld, Low-carbon (Center), and the Material (Bottom), Part B of Fig. 2, That Had Been in Commercial Service. Magnification, all 100X.



Figs. 6, 7 & 8.—Diffraction Patterns Corresponding Respectively to Figs. 3, 4 & 5. Portion A (left) is the "as-cast" metal and Portion B (center) is the weld metal.

ing a piece of high carbon 65 per cent Ni, 15 per cent Cr alloy which had not been in service, (part A), welded to a piece of similar alloy, (part B), that had been in commercial service for several thousand hours. The welding rod used was a commercial coated rolled rod of low carbon 65-15 alloy. Ordinary shop practice was used in making the weld. Figs. 3, 4, and 5 are photomicrographs of the as-cast material, the weld, and the material that had been in commercial service respectively. The grain boundaries are clearly brought out in the low carbon weld metal.

The diffraction patterns, Figs. 6, 7, and 8, corresponding to Figs. 3, 4, and 5, indicate that the as-cast material has larger grains than the weld metal and that the weld metal has larger grains than the material that had been in service. The diffraction pattern and the photomicrograph of the weld metal are similar to what we would expect to find in other metals having about the same grain size. Obviously the photomicrograph of the as-cast material, Fig. 3, and the corresponding diffraction pattern, Fig. 6, are not in agreement if we assume that the carbides delineate grain boundaries. However, the diffraction patterns appear to be in fair agreement with the macro etch, Fig. 2.

By etching with a mixture of chromic and hydrochloric acids, (5 parts 10% aqueous chromic acid solution, 25 parts concentrated HCl), and using polarized light, Dr. Forgeng of the Union Carbide & Carbon Research Laboratories was able to obtain photomicrographs showing the true grain size of these alloys. Fig. 9 shows portions of three grains in the as-cast material. Fig. 10 is a photomicrograph of the material that had been in service, part B, taken with ordinary illumination, and Fig. 11 is the same field taken between crossed nicol prisms. These results are in excellent agreement with the diffraction patterns.

Effect of Carburization

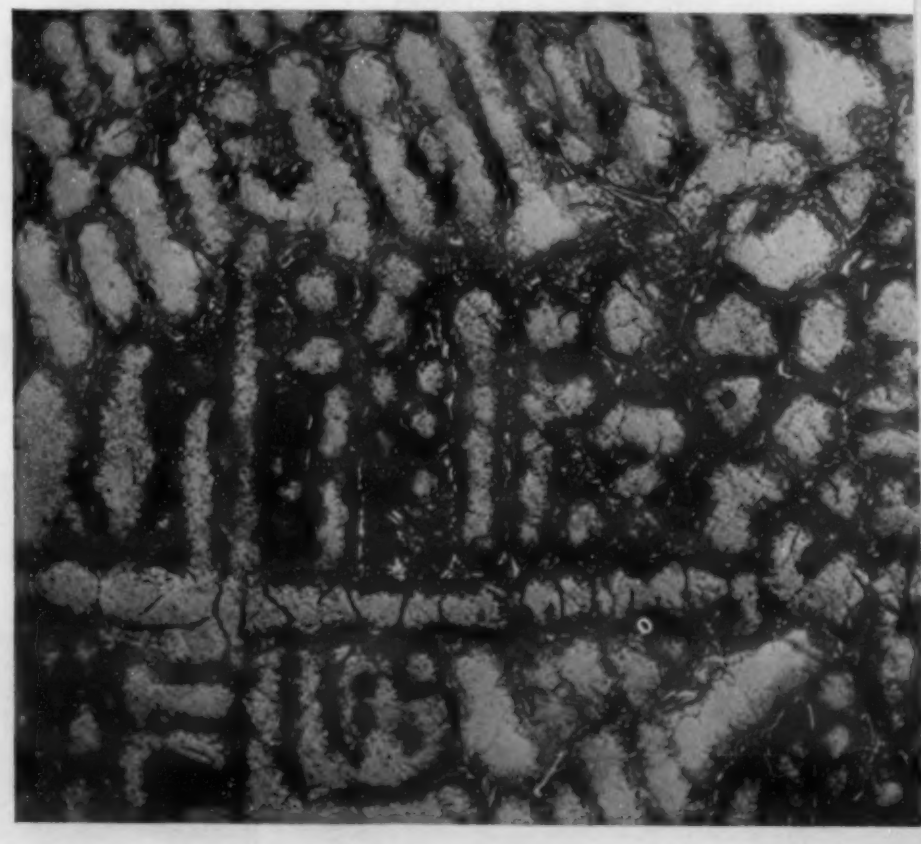
In studying the effect of carburization, it has been noted that probably the most drastic non-destructive change in the microstructure of the high nickel-chromium alloys is that which occurs in the thin layer of metal which has been in direct contact with the carburizing medium for a long period of time. This change is shown in Figs. 12 and 13 representing a casting that had been in commercial service for 8,500 hrs. Not only is there an actual penetration of carbon for a short distance, Fig. 12, but the original carbides are broken up and rearranged throughout the section. The carbon content of the inside surface is 1.53 per cent and that of the outside surface 0.53 per cent. The diffraction patterns, Figs. 14 and 15, show that the penetration of carbon has very little if any effect upon the grain size. Fig. 16 is a photomicrograph taken near the carburized surface showing the true grain size.

Conclusions

In view of the above facts, we may draw the following conclusions.

1.—The carbide network does not necessarily bear any relation to the actual grain boundaries in the high carbon

Fig. 9.—Portions of Three Grains in the As-Cast Metal of Fig. 2. Magnification 100X.



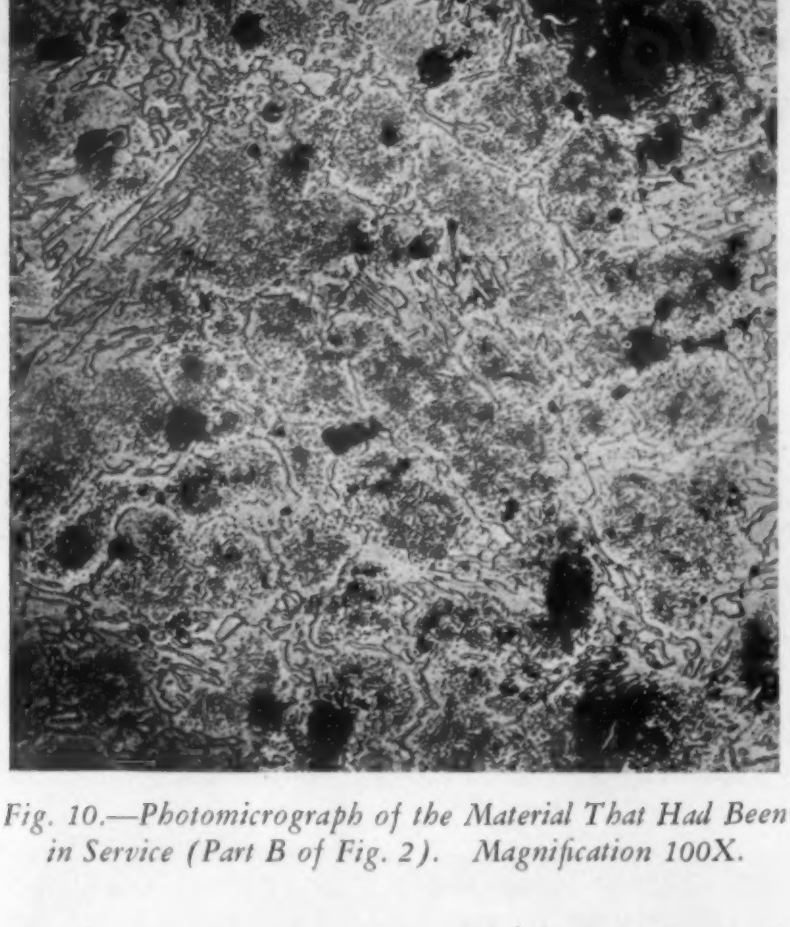


Fig. 10.—Photomicrograph of the Material That Had Been in Service (Part B of Fig. 2). Magnification 100X.

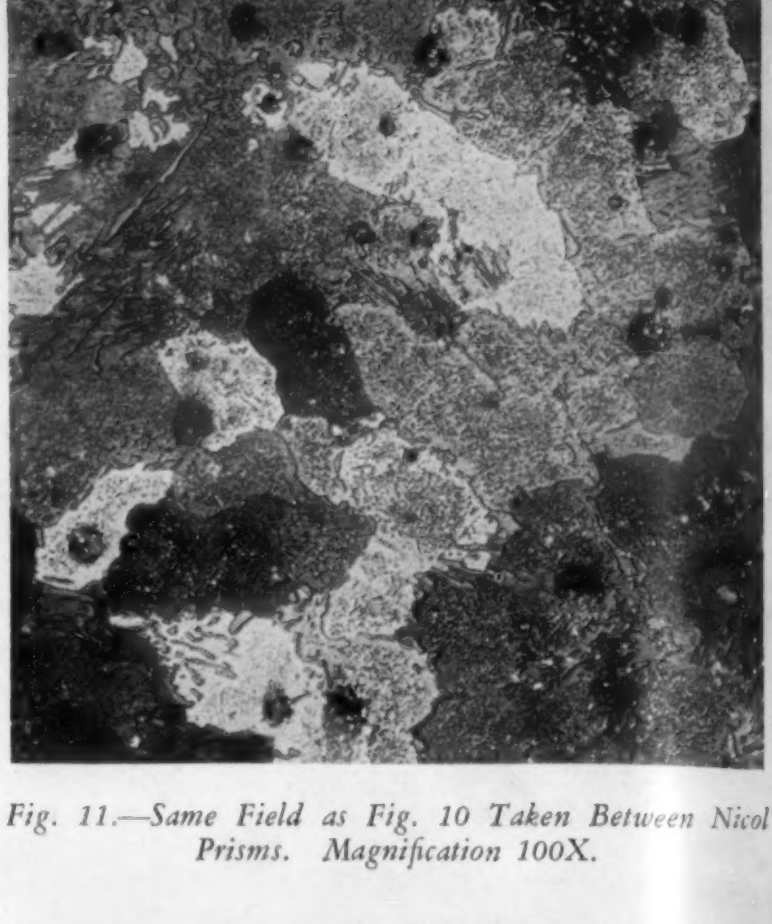


Fig. 11.—Same Field as Fig. 10 Taken Between Nicol Prisms. Magnification 100X.

cast alloys. A few apparent exceptions have been noted in which grain boundaries appear to follow the carbide network. Conditions of this kind are more prevalent around areas of high casting stress and are probably minute hot tears caused by the concentration of stress within the grain.

2.—After being subjected to high temperatures for long periods of time, these alloys undergo considerable change in their microstructure. The original network structure is broken up, resulting in a random distribution of carbides. There are indications that the grains undergo slight fragmentation over long periods of time in commercial service. This is indicated by the increase in the number of doublets and radial asterism in the diffraction patterns. Furthermore, the migration of carbides under service conditions and the increase in the number of carbides due to the absorption of carbon under carburizing conditions do not appear to have any marked effect on the true grain size of

Fig. 12.—Structure Near Outside of Casting, Exposed to Furnace Atmosphere. Magnification 100X.

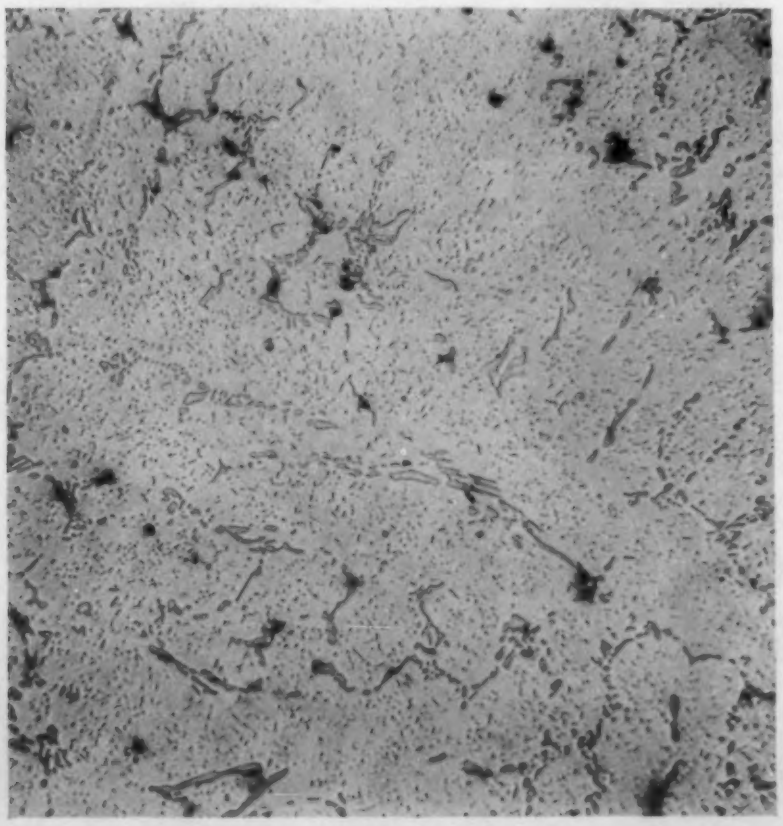
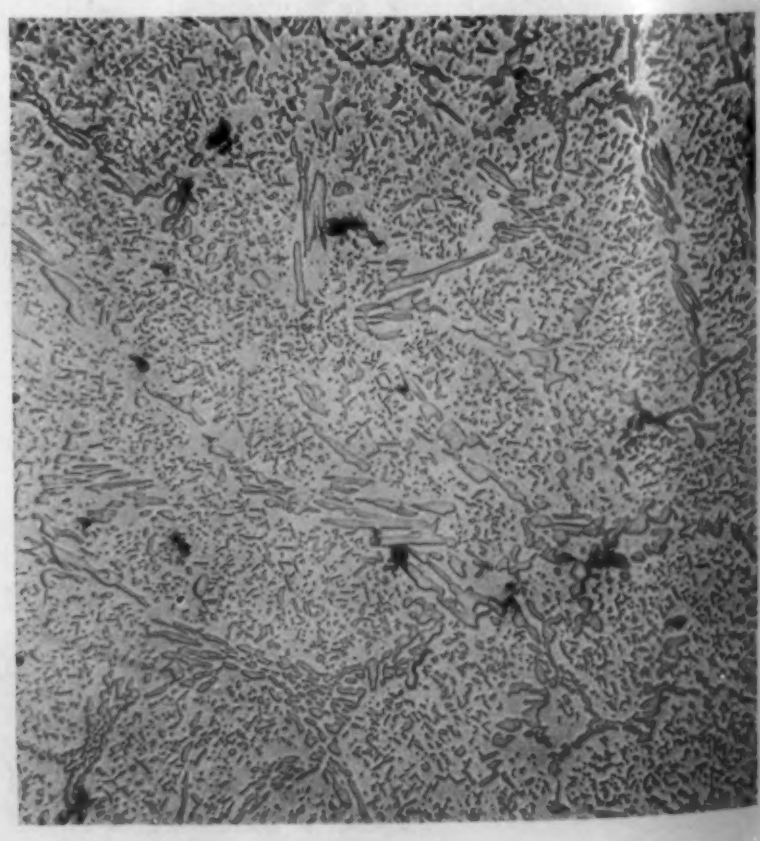


Fig. 13.—Structure of Highly Carburized Inside Layer of Casting. Exposed to Carburizing Gases for 8500 hrs. Magnification 100X.



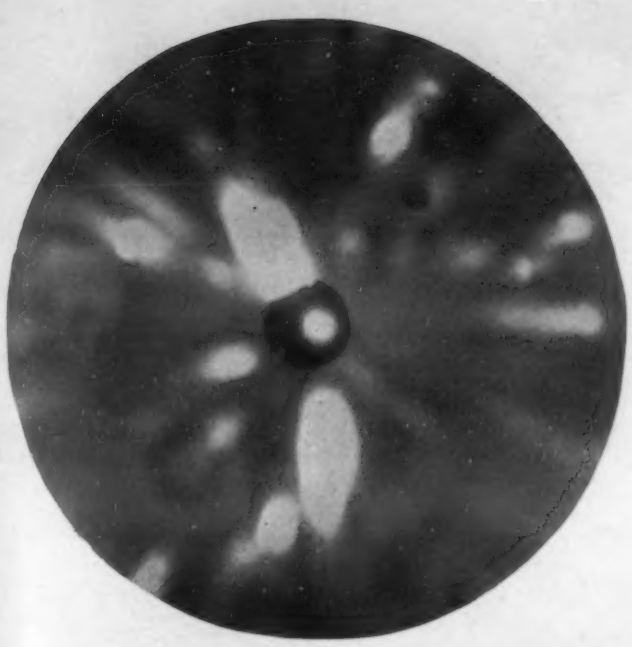


Fig. 14.—Diffraction Pattern of Same Area as Fig. 12.

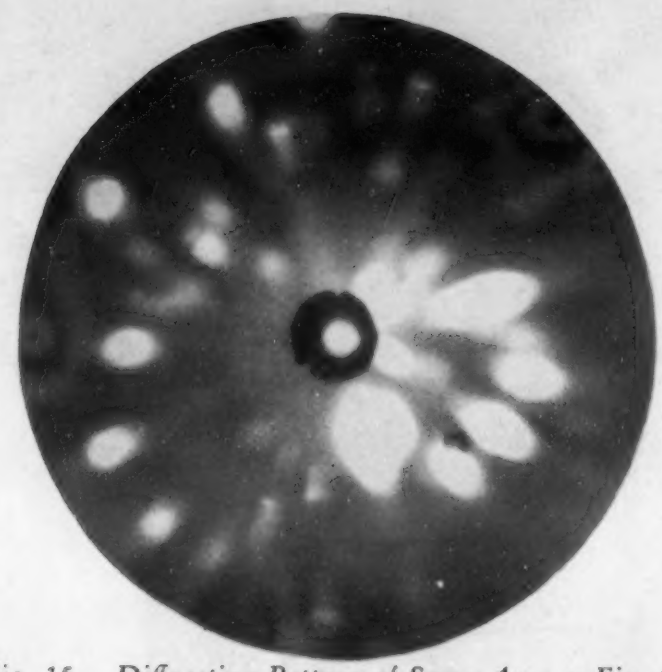


Fig. 15.—Diffraction Pattern of Same Area as Fig. 13.

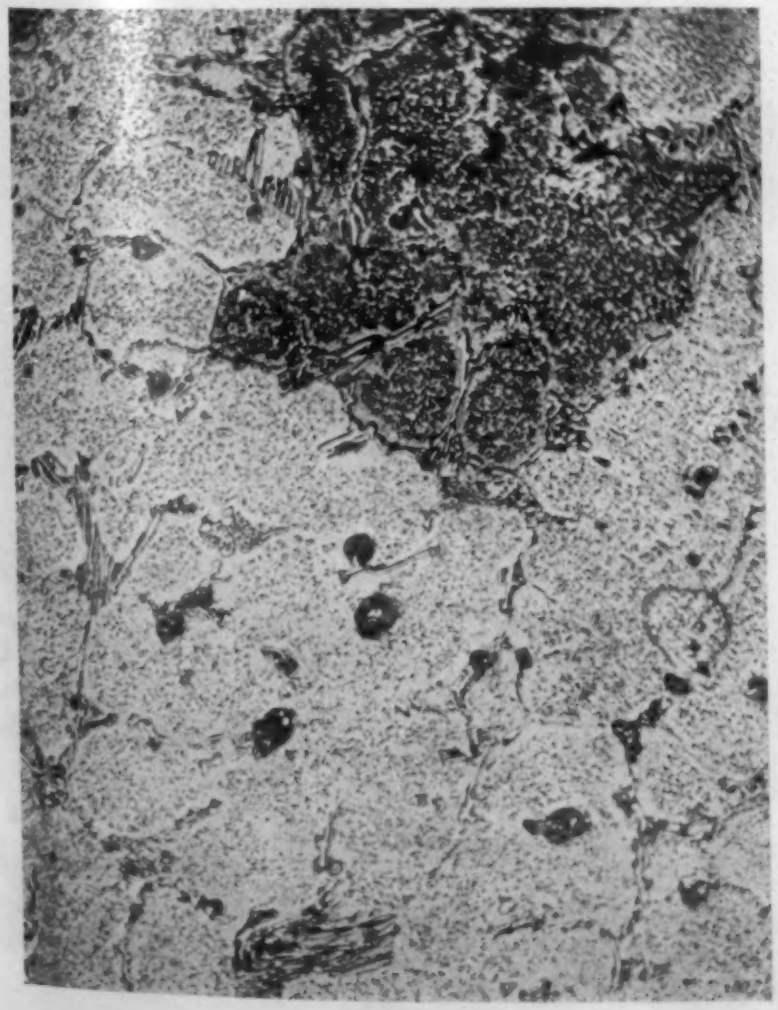
these alloys. This supports the theory that the carbides, which are probably nothing but interdendritic filling, have little direct relation with the true grain boundaries of the cast high nickel-chromium alloys.

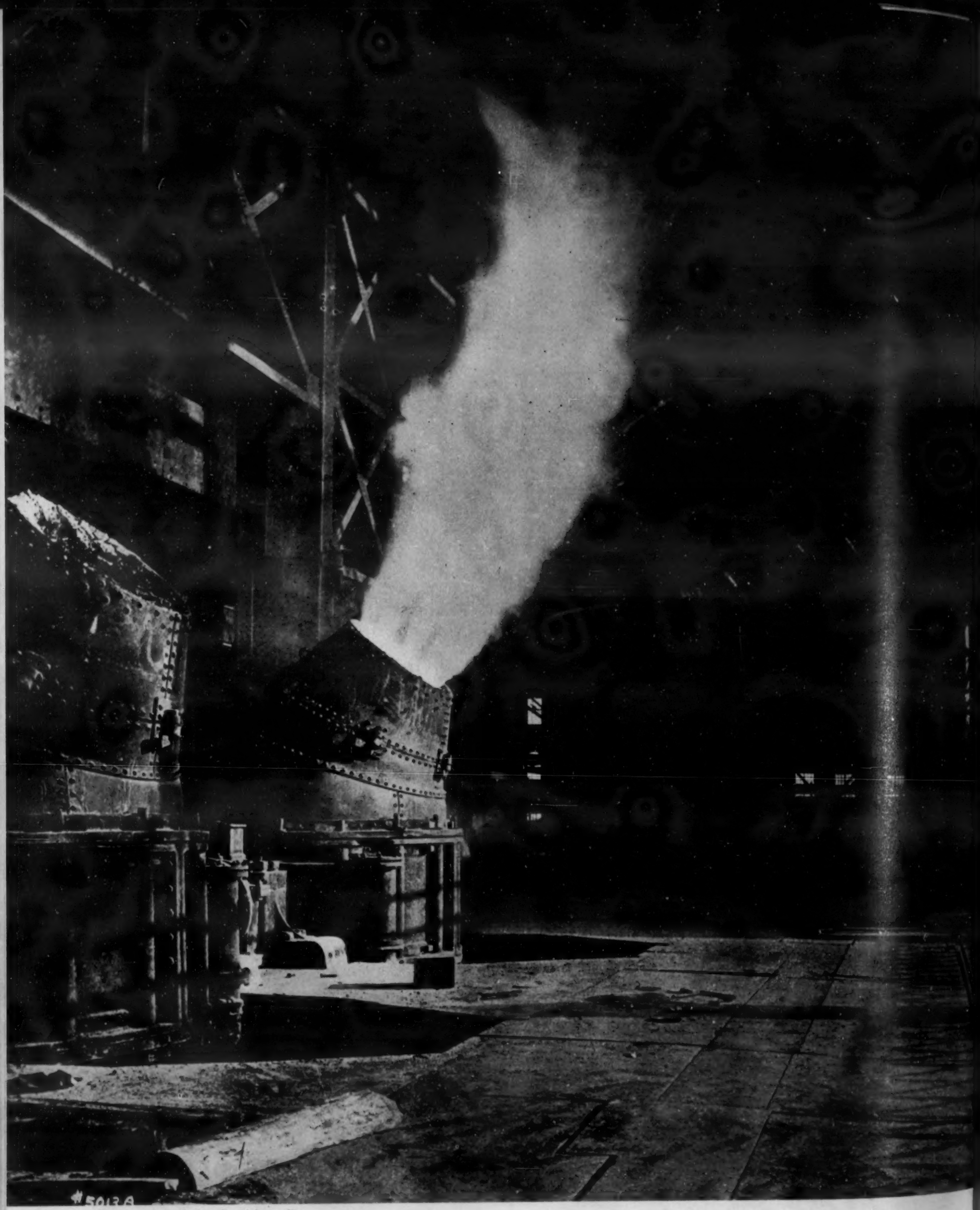
3.—Etching methods aimed to bring out carbides do not show the true grain boundaries in the cast alloys. While it has been possible to bring out different grains within certain specimens by using the hydrochloric acid-ferric chloride etch, the results are not reliable because the individual grains are stained unevenly and their boundaries are not always attacked. This etchant gives best results on material that has been in service for some length of time.

4.—It is apparent that the grain size of the cast nickel-chromium alloys is very large and that lower magnifications than 100 diameters should be used. In fact, for the thicker sections, a macro etch will give satisfactory visual information in many instances. For microscopic grain size determinations, the CrO_3—HCl acid etch and crossed nicol prisms method suggested by Dr. Forgeng are recommended.

Of the accompanying illustrations, the following were made by the Union Carbide & Carbon Research Laboratories, Figs. 3, 4, 5, 9, 10, 11, and 16. The authors acknowledge with thanks the assistance of Dr. Forgeng for his comments and his preparation of these illustrations.

Fig. 16.—Photomicrographs of Same Area as Fig. 13. Taken Near the Carburized Surface Showing the True Grain Size. A (left) is ordinary illumination and B (right) taken with Nicol Prisms.





Courtesy: Bethlehem Steel Co., Bethlehem, Pa.

Bessemer Converter in Operation

MECHANICAL PROPERTIES OF

Four Binary Tin Bronzes—I

AT ROOM AND ELEVATED TEMPERATURES

by Claus G. Goetzel

Metallurgist, Hardy Metallurgical Co., New York

ALTHOUGH THE BINARY TIN BRONZES are among the best known copper alloys, and have been commonly used since antiquity, our knowledge of their general characteristics and of their best performance is still rather sketchy. For this reason alone, any examination of their properties, however systematic, should be welcome; the real purpose of the work reported here, however, was to establish a reliable means of comparison between four standard tin bronzes and other bronzes, and so to construct a suitable base line for study of the more complex alloys in which tin is replaced, partly or completely, by aluminum, silicon, manganese, zinc or lead.

The materials studied were binary tin bronzes of copper-tin ratios 94/6, 90/10, 86/14 and 80/20 (German Standard Bronzes WBz 6, GBz 10, GBz 14 and GBz 20, respectively). The alloys, prepared according to the German Industrial Standard DIN No. 1705, pages 1 and 2, were examined in the cast condition and after annealing; the study of the 94/6 bronze, nominally a rolled material, was included merely for comparison purposes. Data were secured on elastic limit, proportional limit, yield strength, tensile strength, elongation, etc. at room temperature and at 100, 200, 300, 400 and 500 deg. C.; the Brinell hardness was measured at room temperature and at 100, 200 and 300 deg. C.

Preparation of Samples

The following metals were used in preparing the alloys: Electrolytic copper (0.001 Pb, 0.0004 Bi, 0.003 H_2, 0.004 Fe, 0.0025 per cent Ag, trace As); Straits ("Banca") tin (0.02 Fe, 0.02 Cu, 0.02 Pb, 0.02 Sb, 0.02 per cent As); phosphor-copper, (1 per cent P, commercial).

Melting and Casting

A 90 kg. charge of each of the four alloys was melted down under a protecting cover of charcoal in a forced draft coke furnace. In order to obtain identical alloys a double melting process was used; after the first melt the alloys were cast into ingots in iron molds and these ingots were then remelted. For each charge 0.011 to 0.045 per cent P was added as a deoxidizer, during both of the melts.

The physical tests required the casting of 24 tensile specimens for each of the four alloys. Twelve raw cast rods had to be cast from each alloy; from each raw cast rod one cast and one annealed specimen were obtained. These rods had a diameter of approximately 1 in. and a length of approximately 15 in. The forms were made in such a manner that each mold consisted of four raw cast rods. The molds were horizontal sand molds, constructed with large gates ($3\frac{1}{2}$ in. in diameter, 4 in. high) and equally large risers (4 in. in diameter and 4 in. high). The opening between the rods and the gates (inlet) had the same diameter as the rods themselves, so that pipes and shrinkage in the raw cast rods were avoided. The inlet became considerably thicker towards the gates and towards the risers.

The molding material was the sand customarily used in foundries for molds. The molds were dried for approximately 18 hrs. at about 350 deg. F. and the metal was poured while they were still warm. The graphite crucibles were carried to the molds and the alloys cast slowly and with medium stream while the metal was very hot, (approximately 2300 deg. F.) After casting the gates and risers were immediately covered with a handful of charcoal, in order to promote a suction of the casting out of the gate and riser.

When they had cooled, the castings were carefully marked, and the gates and risers cut off. The castings and scrap materials were reweighed, and chemical analyses were made of the four alloys. The results are shown in Table I.

Annealing Treatment

The annealing treatment was as follows: Each of the raw cast rods were sawed into two tension test specimens and one slug for Brinell hardness tests. Half of the samples were annealed in an electric furnace according to the scheme shown in Table II. The temperatures and the time of annealing were selected from practical experience. The rods were allowed to cool slowly in the furnace.

Table I. Results of the Chemical Analyses

Material	Cast-bar	Analyses after Test I: Button Test Cu %	Sn %	Pb %	Mixture of Sawings Sn %	P %
WBz 6 (94/6)	1	94.40	5.45	0.13	6.26	0.021
	2				6.57	
	3				6.72	
	average	94.40	5.45	0.13	6.52	0.021
GBz 10 (90/10)	1	90.90	9.09	....	10.22	0.012
	2			....	10.28	
	3			....	10.40	
	average	90.90	9.09	....	10.30	0.012
GBz 14 (86/14)	1	86.05	13.90	trace	14.09	0.018
	2				14.15	
	3				14.16	
	average	86.05	13.90	trace	14.13	0.018
GBz 20 (80/20)	1	80.00	19.95	....	20.50	0.038
	2			....	20.55	
	3			....	21.23	
	average	80.00	19.95	....	20.76	0.038

Mechanical Treatment

The shape chosen for the tension test pieces is shown in Fig. 1. The specimen had a diameter of 10 mm and a gage length of 100 mm and was threaded at each end. (The test piece did not correspond to the standard of the A.S.T.M.) The specimens for the tension tests at elevated temperatures received a special machining. All specimens were cleanly turned down but not ground. They were subdivided into 20 divisions each 0.5 cm., in a special subdividing machine, in order to get accurate measurements of the elongation on the ruptured test pieces. The Brinell slugs were prepared for the tests by grinding and polishing the two cut surfaces parallel to each other. For the Brinell tests at elevated temperatures the slugs were turned down to 24 mm and machined to a special shape, so that they could fit into the testing device.

Testing Equipment and Procedure

The average of at least five tension tests of the cast and also five of the annealed test pieces were taken for each alloy. The machine for the tension tests at room temperature was a "Mohr & Federhaff" five-ton tension machine with hydraulic drive and automatic pendulum weight adjustment. The elongation of the test pieces up to the yield point was measured by means of the Martens' optical precision extensometer and from then on with a per cent scale attached to the test piece. The experiments were conducted in accordance with the standard methods of the A. S. T. M.

Stress-strain values were plotted for each sample, according to the method approved by the A. S. T. M.; the individual curves, which cannot be shown because of their great number, permitted in each case the location of the various yield points such as the 0.003 per cent elastic limit, the 0.02 per cent (first) and the 0.2 per cent (second) yield points. On the broken test pieces, the elongations were determined according to the German Standard Regulations DIN No. 1650, page 1. The average elongation away from the fracture (symmetrical elongation) and the elongation at the fracture (constriction elongation) were also determined, but appear of minor importance. The reduction of area was determined and exact observations

Table II. Heat Treating Data of the Rods

Material	Annealing Temperature, Deg. C.	(Deg. F.)	Annealing Time approximately, min.
WBz 6 (94-6).....	900	(1652)	30
GBz 10 (90-10).....	780	(1468)	300
GBz 14 (86-14).....	780	(1468)	360
GBz 20 (80-20).....	780	(1468)	420

were taken of the ruptured specimens with regard to surface conditions and the fractures.

In order to obtain an exact idea of the static mechanical properties of the four bronzes at elevated temperatures, a tension test on an "as cast" piece and on an annealed test piece was made from each alloy at 100, 200, 300, 400 and 500 deg. C., to which supplementary tests were added as far as it was necessary. For these tests a 50-ton tension testing machine constructed by Martens with a hydraulic drive and beam arm weight adjustment was used. As an elongation measuring device, a Martens mirror extensometer was again used in these tests, up to the yield point. With the exception of changes in construction, the device consisted principally of a different measuring spring equipment. "Nichrothermsteel" (similar to Invar) was used in the construction of the optical precision extensometer for these tension tests at elevated temperatures, for the measuring springs, rings, etc., because of the heat effects. The electric furnace used was so attached as to be an integral part of the testing machine during each test. The heating coil was wound on a quartz pipe and was divided into an upper and a lower heating coil so that the testing temperature could be accurately regulated. A protecting perforated iron tube was placed inside the quartz pipe to prevent damage of the latter at rupture, and the test piece itself was screwed into double sockets within the protecting tube.

Except for the size of the tensile specimens and the testing temperatures, the procedure corresponded to the regulations of the A. S. T. M. The uniformity of temperature over the gage length, and sufficiently beyond to bring the elongation during testing all within the zone of uniform

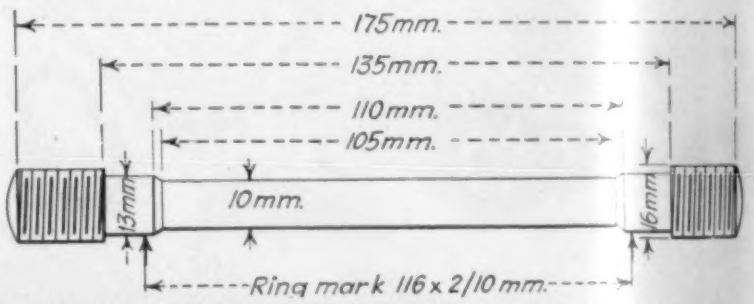


Fig. 1—Shape and Dimensions of Test Specimen.

temperature, was given and covered also the A. S. T. M. regulations. The thermocouple hot-junctions were attached to the upper and lower end of the gage length and were protected by asbestos pads from direct radiation from the heating coils. The temperature difference between the upper and lower end of the specimens in no case exceeded 3 deg. F., and the range of the testing temperature was always within 8 deg. F. These close ranges were made possible by using an upper and a lower heating coil, so that the testing temperature could be accurately regulated. The heating coils were controlled by a precision ammeter and were manually regulated during a heating period of at least 1 hr. by resistances.

During the tests the specimen first was loaded to approximately 80 per cent of the expected yield load; then the load was released and again the specimen loaded to approximately 85 per cent. Thereafter the load was released and for each successive loading an additional 5 per cent added, until the 0.2 per cent limit was exceeded. At each load step, the reading was taken after 2 min. of waiting, then, after the load was released, a reading was taken 30 sec. later. This was necessary in order to allow sufficient time for the stretching of the material.

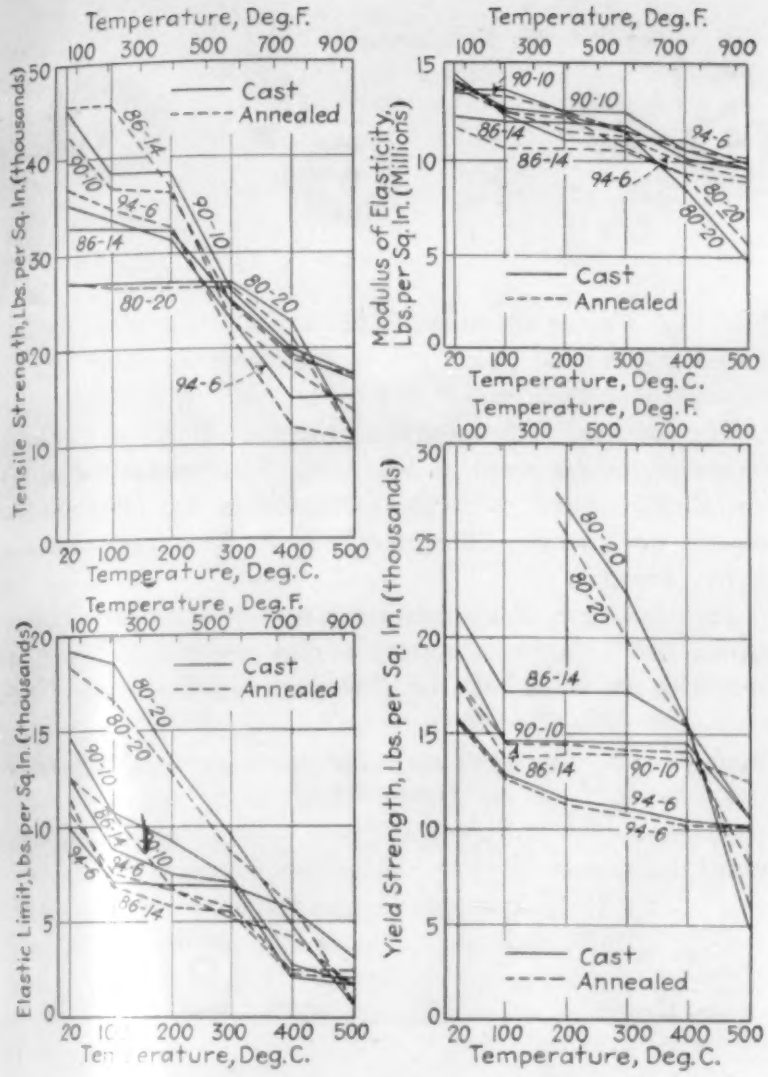
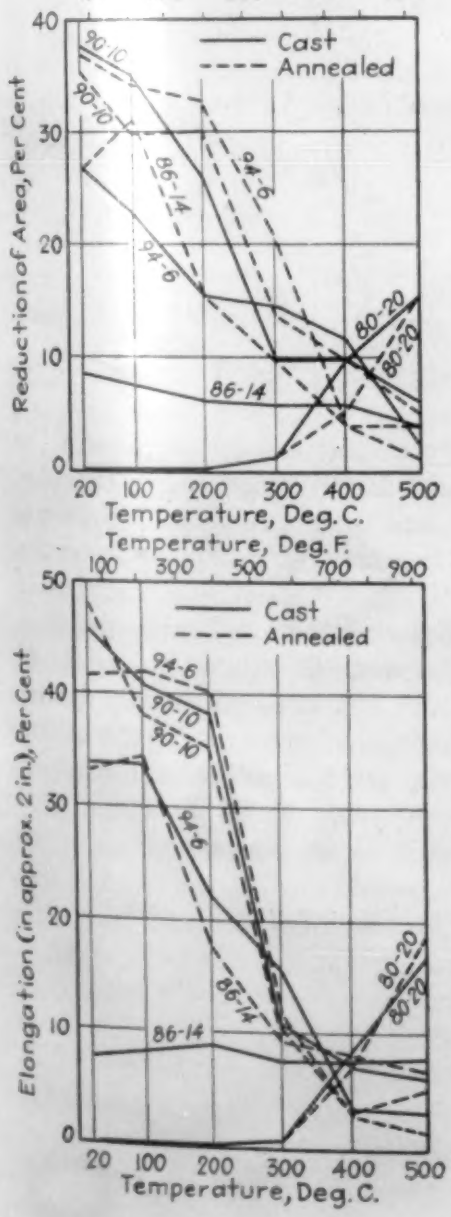


Fig. 2—Mechanical Properties as Affected by Temperature.



The tension tests were not started until the desired test temperature was obtained and constantly maintained and the heat had been completely balanced in all parts of the measuring apparatus. Measurement of the elongation after exceeding the yield point was not possible in the tension tests at elevated temperatures since the test specimens were completely enclosed in the furnace and it was not possible to attach a percentage measuring scale. The static mechani-

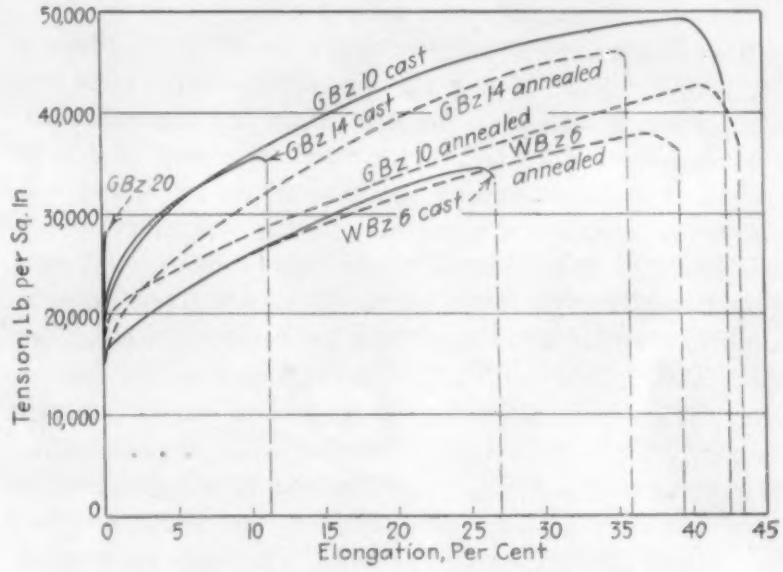


Fig. 3—Stress Strain Curves of Typical Samples.

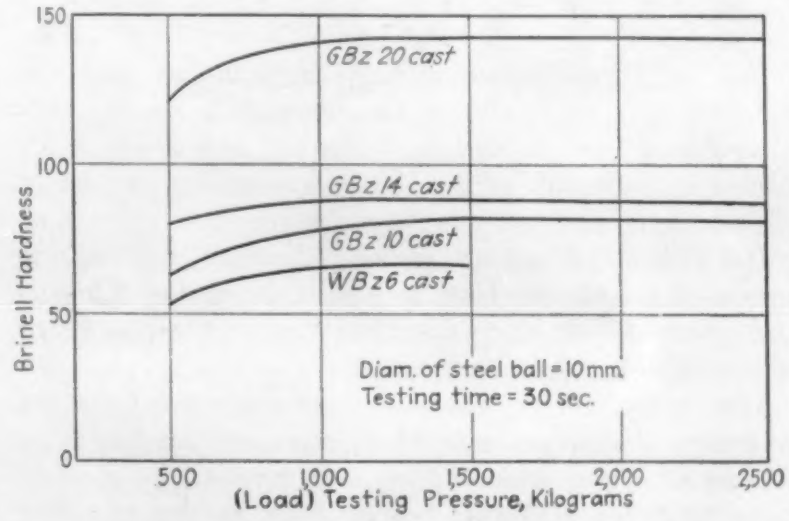


Fig. 4—Brinell Hardness as a Function of Load.

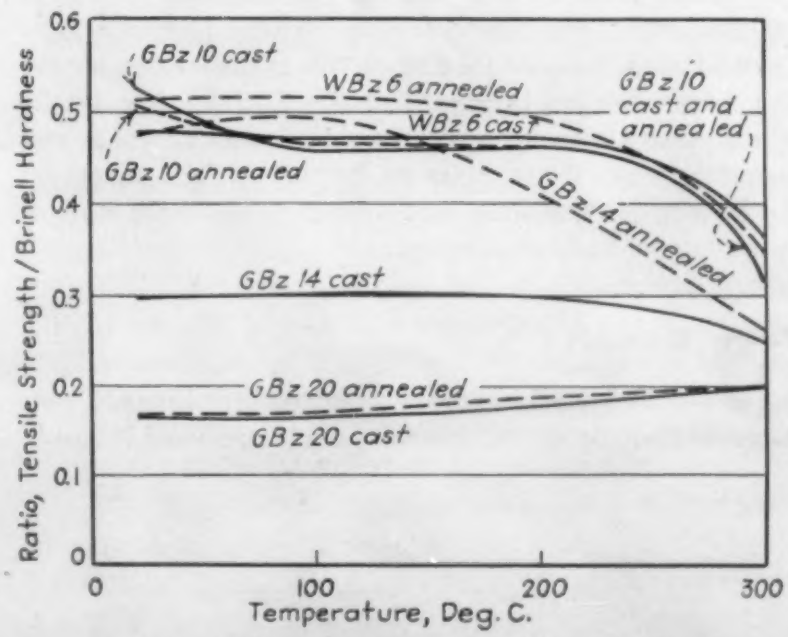


Fig. 5—Ratio of Tensile Strength to Brinell Hardness at Various Temperatures.

Table III. Mechanical Properties of the Four Alloys at Room Temperatures

	WBz 6 (Cu-Sn 94/6)		GBz 10 (Cu-Sn 90/10)		GBz 14 (Cu-Sn 86/14)		GBz 20 (Cu-Sn 80/20)	
	Cast	Annealed	Cast	Annealed	Cast	Annealed	Cast	Annealed
0.2% Yield Strength, lbs. per sq. in.	15645	15645	19913	18490	21335	18490	.....	.....
Tensile Strength, lbs. per sq. in.	35558	36980	45515	42670	32714	45515	27024	27024
Elongation, per cent	32	40	45	47	7	33	0	0
Brinell Hardness	50	51	62	60	79	67	120	117

cal properties were thus determined in the same manner as in the tension tests at room temperature.

Brinell hardness tests were made on all four alloys at 20, 100, 200 and 300 deg. C. The apparatus for these tests was a 3-ton Brinell press made by Mohr & Federhaff, using a hand drive and a weight adjustment by means of a beam arm, and a 20-ton testing machine made by Spiess with manual or mechanical drive and sliding weight beam arm adjustment. The diameter of the testing ball for all tests, was 10 mm. and the testing time 30 sec. At room temperature the test load was varied, 500 kg. being the lowest load used. With this load the hardness of each of the four alloys was determined on an "as cast" and on an annealed sample. On the 94/6 alloy additional tests on cast samples were made with a test load of 1000 and 1500 kg. The other three (casting) bronzes were tested as cast samples with a test load of 1000, 1500 and 3000 kg. The loads corresponded, with the exception of the load of 1000 and 1500 kg., to the regulations of the A. S. T. M., namely $P = 5\ d^2 = 500$ kg. and $P = 30\ d^2 = 3000$ kg., where d is the diameter of the steel ball.

For the Brinell tests at elevated temperatures, heat was supplied by a small electric furnace with 2 heating coils wound on a 1-in. quartz pipe. The test ball was centrally guided in the middle of the pipe by a small holding device made of tin. The ball was placed between 2 samples to be tested with tested surfaces facing each other, and pressure applied to the samples from both sides, using steel cylinders that extended from the furnace and were centered by means of a parallel-faced, heavy steel guide.

The diameter of the spherical impressions was measured by means of a microscope which accurately read to hundredths of a millimeter. Heat was supplied by a small electric furnace with two heating coils so that the heat could be better controlled. To determine the testing temperatures, which were constantly maintained for 5 min. before the test was started, one hot junction each was used for the upper and lower samples. These junctions were clamped into the small holes at the planed sides of the specimens. The test ball was centrally guided in the middle of the quartz tube by a small holding device, which was placed between the samples to be tested. The diameters of the impressions were determined in the same way as in the tests at room temperature.

Test Results

The chief mechanical properties of the four binary Cu-Sn alloys studied at room temperature are summarized in Table III. Fig. 2 gives an assembly of curves of the main values of the mechanical properties of the alloys at room and at elevated temperature.

The mechanical properties of the four alloys at elevated temperatures are given in Table IV. The tension values of the alloys showed, with the exception of the alloy Cu-Sn 86/14, no essential difference between their cast and annealed forms.

Fig. 3 shows a comparison between strain-stress diagrams, based on typical examples of a cast and an annealed specimen of each of the four tested alloys. In these

Table IV. Mechanical Properties of the Four Alloys at Elevated Temperatures

	20°C. (68°F.)	100°C. (212°F.)	200°C. (392°F.)	300°C. (572°F.)	400°C. (752°F.)	500°C. (932°F.)
WBz 6 (Cu-Sn 94/6)						
0.2% Yield Strength, lbs. per sq. in.	15,645	12,801	11,379	11,379	11,379	9,956
Tensile Strength, lbs. per sq. in.	35,538	34,136	31,291	22,757	14,223	15,645
Elongation, per cent	33	32	22	16	3	3
Brinell hardness	52	51	47	44	..	..
GBz 10 (Cu-Sn 90/10)						
0.2% Yield Strength, lbs. per sq. in.	19,913	14,223	14,223	15,645	14,223	11,379
Tensile Strength, lbs per sq. in.	45,515	38,403	38,403	25,602	19,913	17,068
Elongation, per cent	45	39	32	10	6	6
Brinell hardness	62	60	59	57	..	..
GBz 14 (Cu-Sn 86/14)						
.2% Yield Strength, lbs. per sq. in	21,335	17,068	17,068	17,068	15,646	9,956
Tensile Strength, lbs. per sq. in.	32,714	32,714	31,291	24,180	19,913	17,068
Elongation, per cent	7	8	9	7	7	8
Brinell hardness	79	77	74	69	..	..
GBz 20 (Cu-Sn 80/20)						
0.2% Yield Strength, lbs. per sq. in.	.....	.....	27,024	22,757	15,645	5,689
Tensile Strength, lbs. per sq. in.	27,024	27,024	27,024	27,024	22,757	11,379
Elongation, per cent	0	0	0	0.5	8	15
Brinell hardness	120	119	110	98	..	..

diagrams one can observe a clear distinction between the ductile materials (94/6 and 90/10 as cast and as annealed, and 86/14 as annealed) and the brittle alloys (86/14 and 80/20 as cast and 80/20 as annealed). Fig. 4 shows the Brinell hardness of the 4 alloys, as cast, as a function of the test load at constant testing time and using the same steel ball of 10 mm. diameter. Of course the values of the soft materials at the high test loads are of only relative importance, since their determination was subject to certain inaccuracies because of the large diameter of impression and displacement of the material. Fig. 5 shows the ratio of tensile strength to Brinell hardness as a function of the testing temperature.

(To be concluded)

Engineering As A Career

by Fred P. Peters

Assistant Editor, METALS AND ALLOYS

RECENTLY A SERIOUS-MINDED, intelligent young friend, his studies at a well-known eastern engineering school one-half complete, sought our advice on a problem that is all too common today. "Why", he asked, "should I continue to study metallurgy when it is apparent that business holds more promise of an interesting and profitable career than does engineering? Engineers as a group are woefully underpaid. Very few of them occupy the really high-salaried jobs in industry—the majority never get beyond the routine unimportant work thrust upon them in the first few years after graduation. It seems to me that we are producing too many engineers for existing needs and opportunities."

A wholly satisfactory answer to his question would have to cover a multitude of points—the justice of his indictment, the value of engineering education, the demand for trained engineers, salary scales and financial opportunities in technical fields, the general future of engineering, etc. Here are parts of the answer that we found in a very hurried survey.

Administration

That the plums on industry's tree have gone, in the past, more frequently to the business-trained than to the technically trained man cannot be denied. This may have been due to management's underestimation of the value of engineers, to the engineer's frequent willingness to work for love rather than money, to lack of professional organization, etc., but most likely it results from the engineer's characteristic inaptitude for other than technical problems and a rather naive conception of social, economic, commercial and political conditions, which has left him incapable of successfully handling large scale enterprises, particularly those involving the general public. In the last few years, however, owing to greater general recognition of engineering usefulness and a broadening of the engineer's training, the engineer has successfully invaded the field of management. Examples familiar to most metallurgists are the careers of E. C. Bain and P. D. Merica.

Recognition of the administrative usefulness of engineers is becoming increasingly widespread. "Business—our national prosperity, depends more and more on the efficiency, the smooth operation of our production machinery. . . . For this reason more and more of the executives I meet are men with an engineering training. More and more are the business owner, the investor and the banker turning the management of industry over to the engineer."[1] Again, "Various studies made by independent groups concur in showing that two-thirds of the engineering graduates are engaged, by the time they have been out of college for 15 yrs., in work that is primarily executive in character."[2] Also, "70 per cent of all engineers apparently gain executive responsibility sooner or later or have it thrust upon them. . . . Engineers have largely become leaders in industry."[3] And finally "To an increasing extent industries, utilities and public works are dependent upon engineering college graduates for the solution of their technological problems, as well as those of an administrative and executive character."[4]

Engineering Education

The importance of the engineer's schooling as preparation for an executive career is obvious, and engineering education is in general being modified to meet the new demands placed on its graduates. The current trend is away from the narrow, specialized, highly technical training, toward broader curricula stressing fundamentals rather than the finest details of specific sciences, and including a greater proportion of 'humanistic" subjects like sociology, economics, psychology, history and English. According to Gilbert E. Doan, "Industry as a whole would prefer engineering graduates of this well-rounded type instead of the premature and narrow specialist which it now receives, and industry has said so in no uncertain terms. Since both the scholars and the industrial leaders are agreed in this matter, the trend is likely to develop rather rapidly."[5] Elsewhere Doan presents a forceful lucid appeal for liberalized technical education, concluding "it (maximum technical training without broad mental growth) is bad for the boys, for the profession, for industry, and for the nation. The specialties should be studied later—when the graduate knows which one of a thousand specialties he wants, not before."[6] Potter observes the disappearance of the specialized technician and his replacement by a graduate with broad fundamental technical background and with greater knowledge of people as individuals and society as a whole. "The providing of a background of engineering knowledge is not being considered as important as development of ability to reason logically and to arrive at truth by observation and analysis."[4]

The value of an engineering education under any circumstances is lauded by President Compton[7] of M. I. T. and Dean Kimball[8] of Cornell. According to their views, a mid-course shift from business to engineering might be reasonable, but the reverse procedure would be ill-advised; both believe that a technical training is excellent prepara-

tion for any career in industry. Says Compton, "Technological education will be increasingly recognized as a most valuable preparation for a satisfactory life in this technological world, as well as the *necessary* training for that large special group who themselves develop, build and operate the world's machinery." And from Kimball, "(The engineer's) superiority as an administrator, other things being equal, lies in his scientific training and his intimate knowledge of industrial operations. When to these is added a knowledge of accounting and finance, the combination is the very best that can be had for work in industrial administration of any kind." Knowles believes it is easier for the engineer to become proficient in administrative skills than for one without scientific training to acquire the latter, while Johnson[9] claims there is no better foundation for a variety of non-technical careers (including the ministry!) than a broad general engineering education. It cannot be denied that a technical training confers mental habits and attitudes of distinct aid to success in administrative fields.

Salaries

We agree with our young friend that salary scales in technical fields are generally too low, but we do not concur in his belief that they are significantly lower than those obtaining among business men with equivalent (in point of time) education. In a survey of the engineering profession recently published by the Bureau of Labor Statistics[10] the average annual salaries in 1934 of engineers that had been out of college more than 10 years were (1) $4100 for men doing engineering work for private companies and (2) $3600 for technically educated men doing non-engineering work; in 1929 these same men had averaged (1) $5200 and (2) $6400. For engineers out of college between 5 and 10 yrs., average salaries in 1934 were (1) $2400 if in engineering work and (2) $1700 if in non-engineering work. Although we have no comparative data for non-technically educated men, our personal observation has been that the foregoing averages are certainly no lower than the incomes of men that obtained B.A.'s at about the same time.

The Bureau's figures, of course, reflect the influence of the depression on engineering salaries, and they are therefore lower than such figures may be a few years hence. It should be noted, however, that the men in engineering fared less badly than did those employed in non-engineering work between 1929 and 1934.

The class of 1925 at Worcester Polytechnic Institute conducted an interesting survey of the income of its members in the 10 yrs. after graduation.[11] This showed that the maximum salary (not the same man throughout) had gone from $2500 in 1925 to $4400 in 1932 to $8200 in 1934; minimum from $900 in 1925 to $1500 in 1934 and the median (20th man on the salary scale) from $1500 in 1925 to $2200 in 1932 to $3000 in 1934. These figures agree roughly with the Bureau's, and show that even through the depression this group of young engineers maintained a generally satisfactory salary level. In both cases the sharp upturn in 1934 is noticeable. It is to be expected that engineering salaries in the future will be higher than for previously comparable groups, owing to the definite trend towards "professionalizing" of engineers and the aforementioned increased recognition of engineering usefulness.

Industry's Needs

Is there a strong current demand for engineers, or are we possibly grinding out technicians faster than industry can absorb them, profitably to all concerned? President Hotchkiss[12] of Rensselaer in a recent article, answers with an emphatic negative and claims that industry is eager for all the well-trained engineers it can get its hands on. In our own field we observe today an acute shortage of metallurgists, so much so that this June found nearly all the well-known schools that graduate mining and metallurgical engineers able to achieve 100 per cent placement, with a greater demand for men than they were able to fill. H. W. Gillett[13] in a recent editorial warned that we are graduating too *few* metallurgists, even if we include the great amount of "good metallurgical raw material in the form of chemists, physicists and engineers" that is always available. This shortage of trained metallurgists is echoed in a very recent survey of career possibilities in metallurgical engineering, which found that starting salaries are high for this reason, and that "the qualified and progressive engineer has better opportunities in metallurgical engineering than in any other engineering field for advancement and the chance to assume executive responsibilities. The field is decidedly *uncrowded* for men of ability."[14]

Metallurgy is among the youngest of sciences, and still teething. The technical opportunities, the "uncharted fields" within it, are legion. In a recent article Gillett[15] listed scores of practical metallurgical problems as yet unsolved, and in concluding, wrote "what we know and utilize is but the tiniest fraction of what we ought to find out and utilize. . . . Much that we now think is true and important won't be so (in 1956), and many problems now unsuspected, will be the center of interest."

It is hard to see that there are less opportunities in engineering today than in recent years, or that the future, in spite of hesitation in some quarters induced by political trends, will not offer an even greater field for service and profit to the engineer with the proper training. It would indeed be a tragedy for any technically inclined young man to abandon his real interest because he deems it lacking in career possibilities. His ultimate success in any line, of course, will depend on his own vision, ability and continued study, but it is certain to be aided rather than hindered by an engineering education.

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Metallurgical and Commerce News

BY THE EDITORS

Very Heavy Manganese Ore Imports

Imports of manganese ore in 1936 almost established a new record—they approached very close to the record imports of 1926. According to official Government data the manganese ore imports —ore containing approximately 50 per cent manganese and known as metallurgical ore—the record for 1936, compared to a period of years, is as follows in gross tons of manganese content including 1937 to date:

Year	Total Imports	Tons per Month
1925	610,131	50,840
1926	708,400	59,000
1927	617,700	51,400
1928	419,600	34,900
1929	648,800	54,000
1930	562,600	46,900
1931	490,600	40,885
1932	110,634	9,220
1933	288,187	26,015
1934	341,338	28,445
1935	383,500	31,960
1936	706,607	58,800
1937 (5 mos.)	188,175	37,635

Thus at 58,800 tons per month for 1936, the imports just fell short of the record of 59,000 tons monthly in 1926 and exceeded by a considerable margin the 1929 imports of 54,000 tons each month.

With the returns for five months of 1937 available, the rate this year is small but will probably be increased by the inflow in later months.

The extent of the recovery in the steel industry since the bottom of the depression in 1932 is reflected by these imports—an expansion from only 9,220 tons per month in 1932 to 58,800 tons in 1936 or an increase of over six fold. As the steel ingot production expands, the imports of ore for the production of ferromanganese must also increase.

New Steel in the United Kingdom

A discovery of a new steel known as "Stayblade Max" is reported to have been made in the United Kingdom, according to Consul H. M. Wolcott, in the *Iron and Steel Fortnightly*. It is said to be suitable for working at temperatures up to and including red heat, to resist oxidation in air or steam up to temperatures as high as 900 deg. C. and to be "quite machinable." It is used for boiler drums, turbines, high temperature reaction vessels and other units of plants which have to operate at high temperatures and stress. It is reported to possess high chromium and nickel contents, and also substantial additions of titanium and aluminum. Its "time yield" value at 550 deg. C. is as high as 9½ tons per sq. in., so it is suitable for working under fairly severe stress at high temperatures, according to our information. It is of the austenitic type, and can be formed into various sections. In fact, it is already being tried in high temperature turbines in the form of blading, it is stated.

Consumption of Ferrous Scrap and Pig Iron in the United States in 1936

Domestic consumption of iron and steel scrap amounted to 36,469,000 gross tons in 1936, an increase of 38 per cent over 1935, according to preliminary figures compiled by the Bureau of Mines. Total consumption of pig iron amounted to 29,778,000 tons or 44 per cent above the previous year. The use of pig iron as a raw material in the manufacture of steel increased 46 per cent in 1936 whereas the quantity of scrap charged directly to steel furnaces increased only 38 per cent. Likewise the increase in the use of home scrap in steel making was more pronounced than that of purchased scrap.

The net effect of the relatively greater use of pig iron and home scrap in 1936 was to reduce slightly the proportion of purchased scrap in ferrous materials charged to steel furnaces from 26.4 per cent of the total in 1935 to 24.6 per cent in 1936. Production of steel ingots increased 40 per cent in 1936. Exports of scrap continued at a high rate but were 8 per cent below the record shipments of 1935. Prices of iron and steel scrap were materially higher in 1936, reflecting the larger domestic demand as well as the heavy export trade. Preliminary figures given herein for consumption of ferrous materials in 1936 are based on reports from concerns accounting for over 95 per cent of the total consumption. Consequently, in view of the large coverage, final figures to be released at a later date should not show any substantial revisions.

Trends in Actual Steel Exports

A critical analysis of our steel export data reveals an interesting fact—the totals by no means indicate actual sales abroad of finished and other important manufactured steel products. The total exports of pig iron, ferroalloys, rolled and finished steel, and castings are obtained by subtracting from the total export figures, as given officially, the amount of scrap exported. The data thus compiled and handled are as follows for 1937 and for the six previous years in gross tons:

Year	Total Exports	Scrap Exports	Actual Exports	Tons per Month
1931	968,992	136,125	862,867	71,900
1932	594,650	227,522	367,128	30,600
1933	1,341,137	773,406	567,731	47,310
1934	2,832,764	1,835,554	997,210	83,100
1935	3,067,336	2,107,814*	959,522	79,960
1936	3,162,694	1,941,031*	1,221,663	101,805
1937 (5 mos.)	2,790,426	1,651,934*	1,138,492	227,698

* Includes tin plate scrap.

Thus the exports of all the manufactured steel and iron—or *actual steel* exports—were down to 30,600 tons per month in 1932, the bottom of the depression. The extent of the general world recovery, as judged by such exports, is reflected in the monthly exports for 1937 of over 227,690 tons. The gradual recovery is also shown by the monthly data.

American Lead Industry in 1936

The output of refined primary lead from domestic ore in the United States in 1936 amounted to 387,698 net tons valued at $35,668,000, according to the United States Bureau of Mines, compared with 310,505 tons valued at $24,840,000 in 1935, increases of 25 per cent in quantity and of 44% in value. The production of refined lead from foreign sources amounted to 11,458 tons, principally from Peru, Newfoundland and Canada, compared with 14,055 tons in 1935. The total output of primary lead from domestic and foreign sources was thus 399,156 tons in 1936, an increase of 23 per cent over the output of 324,560 tons in 1935. The principal sources of production in the United States were again Missouri, Utah, and Idaho.

Demand for Foreign Spiegeleisen Expands

Demand for foreign spiegeleisen has expanded recently to such an extent that the imports for the last two years exceed those of any years for some time.

The following table, compiled from Government statistics, furnishes a record of the imports of spiegeleisen since 1929 inclusive —in gross tons:

Year	Total Imports	Tons per Month
1929	13,828	1,152
1930	13,406	1,117
1932	8,364	700
1933	26,277	2,190
1934	21,234	1,770
1935	32,375	2,700
1936	52,018	4,335
1937 (5 mos.)	6,637	1,327

With the imports at 4,335 tons per month in 1936 (and 2,700 tons monthly in 1935) there is revealed the magnitude of this movement. In the boom year of 1929 these imports were only 1,150 tons each month. There has been a decided expansion since 1933.

While the American production of spiegeleisen bulks large, the imports are becoming more of a factor in total consumption.

Exports of Steel Scrap At New High

Despite the agitation in the press of the country early this year and the anxiety of many large steel producers, exports of steel scrap continue in a large volume exceeding all previous records. The following table is an analysis of Government export data for scrap iron and steel for a number of years compared with the statistics for this year:

Year	Total Exports	Tons per Month
1926	104,738	8,700
1927	238,303	19,800
1928	516,139	43,000
1929	557,044	46,420
1930	350,499	29,200
1931	135,900	11,325
1932	227,522	18,960
1933	773,406	64,450
1934	1,835,554	152,796
1935	2,103,959	175,330
1936	1,941,031	161,750
1937 (5 mos.)	1,651,934	330,387

At 330,387 tons per month to June 1, this year, the export volume of scrap is now more than double that of 1936. The grand average for the last three years—1934 to 1936—was 163,290 tons per month so that the movement this year is far in excess of that average.

The outgo is still too large. It should be stated that the data here include tin plate scrap.

Very Heavy Output of Ferromanganese

With the sharp upturn in steel production this year, and despite the strikes, there has come a decided increase in the output of ferromanganese by American blast furnaces. The total for the first half has been 170,857 gross tons or 28,476 tons per month. Compared with 1936 and with previous years the authoritative record is as follows in gross tons:

Year	Total Output	Tons per Month
1913	119,493	9,960
1918 (war)	333,027	27,750
1929	335,799	27,820
1930	276,500	23,040
1931	212,115	17,673
1932	57,342	4,780
1933	136,852	11,400
1934	124,190	10,350
1935	185,173	15,431
1936	254,728	21,227
1937 (6 mos.)	170,857	28,476

Thus at over 28,400 tons per month this year to July 1, the ferromanganese production is 34.5 per cent higher than in 1936. The surprising fact is that it surpasses any monthly average in recent years, even exceeding the volume for 1929 and the war record in 1918.

That the output of this important steel making alloy is a measure of the rate of steel ingot output is clearly demonstrated by these data. The ferromanganese production is a barometer of the trend of the American steel industry.

Our Steel Exports Now Back Nearly to Pre-War Volume

An analysis of American steel export data reveals two interesting facts or trends—the present volume shows a gradual increase since the low point in 1932; it is, however, by no means anywhere near the magnitude of that in 1913 or in 1929, just previous to the depression.

Actual, or real, American steel exports are arrived at by subtracting scrap exports from the total outgo. The record therefore for a period of years, as compared with 1913 and with 1929, is as follows in gross tons per month:

Year	Tons per Month
1913	242,300
1929	206,700
1930	135,800
1931	69,400
1932	30,600
1933	47,310
1934	83,100
1935	78,277
1936	101,800
1937 (to June 1)	227,698

From these data it is evident that the low point was the 30,600 tons per month in 1932, generally regarded as the low point of the depression. Since then there has been almost a continual advance, except in 1935. According to the latest available Government data, the present volume has reached over 227,600 tons monthly.

These facts are very encouraging, if compared with previous records. Before the war, our actual steel exports (total reported volume minus scrap) were 242,300 tons per month or only 14,600 tons in excess of the present volume. Compared with the boom year of 1929, present outgo is 21,000 tons in excess of that.

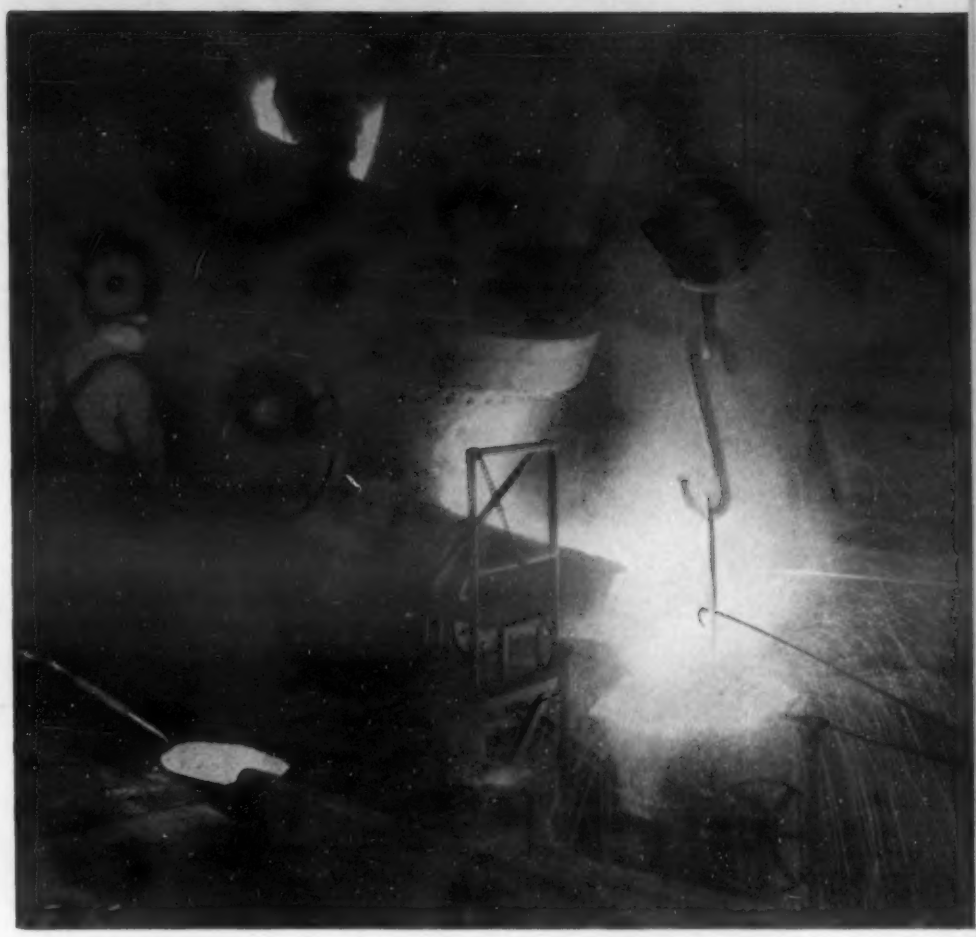
With conditions as they are at present in foreign countries, it is not improbable that these exports will expand rapidly. This has already begun in pig iron

Low Alloy Steel Castings

IN LOGGING AND ROAD CONSTRUCTION

by A. Finlayson

Metallurgist, Pacific Car & Foundry Co., Seattle, Wash.



(A) Pouring Low Alloy Steel from a 3½-Ton Electric Furnace in the Plant of the Pacific Car & Foundry Co.

WE HAVE HEARD A GREAT DEAL during the past two or three years about low alloy structural steels and observed their increasing application to all kinds of riveted and welded assemblies where reduction in weight without loss in strength is the ever present engineering desideratum. Nearly every major company engaged in the manufacture of rolled products is at present promulgating its own special brand of high strength steel and it must be conceded that many of these have fully emerged from the experimental stage and are now demonstrating genuine engineering and manufacturing economies.

Perhaps the Crucible Steel Co. of America and the Jones & Laughlin Corp. may be looked upon as the pioneers in this field. These companies started the trend towards low or medium alloys with the production of higher strength machinery steels in bars, the former with the well known "Maxel" and the latter with "Jalcase". However this may be, properties representing double the elastic strength of mild steel without the sacrifice of ductile qualities are now available in any form from sheets and plates through the entire catalog of rolled shapes and, as above indicated, large tonnages of this material are being consumed, particu-

Fig. 1—A Logging Yarder, Made Entirely of Steel Castings.

Fig. 2—This Caterpillar Tractor Has Its Bulldozer Made of Low Alloy Cast Steel.

larly in the transportation industries in welded assemblies.

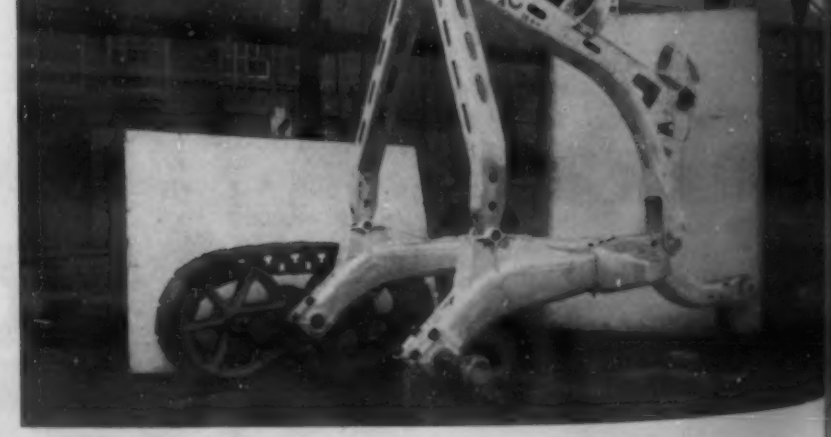
This type of construction is being advocated and in many instances accepted as a substitute for castings, due, in a measure, to a lack of general information in the hands of designing engineers regarding the parallel development of low alloy steel castings which duplicate in all respects the properties and performance of wrought steel products. It is the intention of this article to indicate briefly the service record of a cast steel of this type manufactured by the Pacific Car & Foundry Co. and marketed under the name of "Carcometal."

Logging, road building and general construction are examples of activities which impose the most severe demands upon equipment. Yet it is in such applications that steel castings of the low alloy type have shown unusual endurance, and in many cases proved to be not only the best, but the only satisfactory solution to the unique requirements of design and the extreme demands of loading conditional to their service in the field.

Figs. 1 and 2 are photographs illustrating machinery of this type at work, incorporating such material in the principal members. Fig. 1 shows a logging yarder which resembles nothing so much as a prehistoric monster, working in the fir forests of British Columbia and Washington and, except for bolts and pins, it is made up entirely of castings. The six main castings, namely the boom, struts, reach and fenders, are cast in one piece. Although considerable experimentation and adjustment were required before all of the difficulties encountered in pouring these sections to the specified dimensions had been mastered, they are now manufactured on a production basis entirely free from cracks or cold shuts. Other illustrations show

Fig. 3—A Cast Steel Boom Yarder Assembled Except for the Wheels.

Fig. 4—Another View of the Boom Yarder.



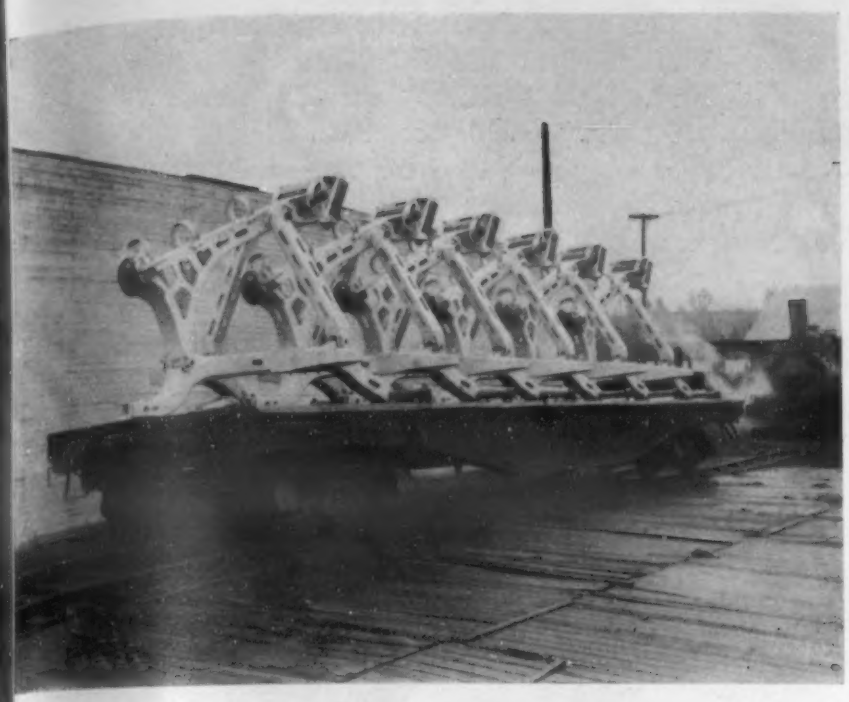


Fig. 5—A Carload of Boom Yarders.

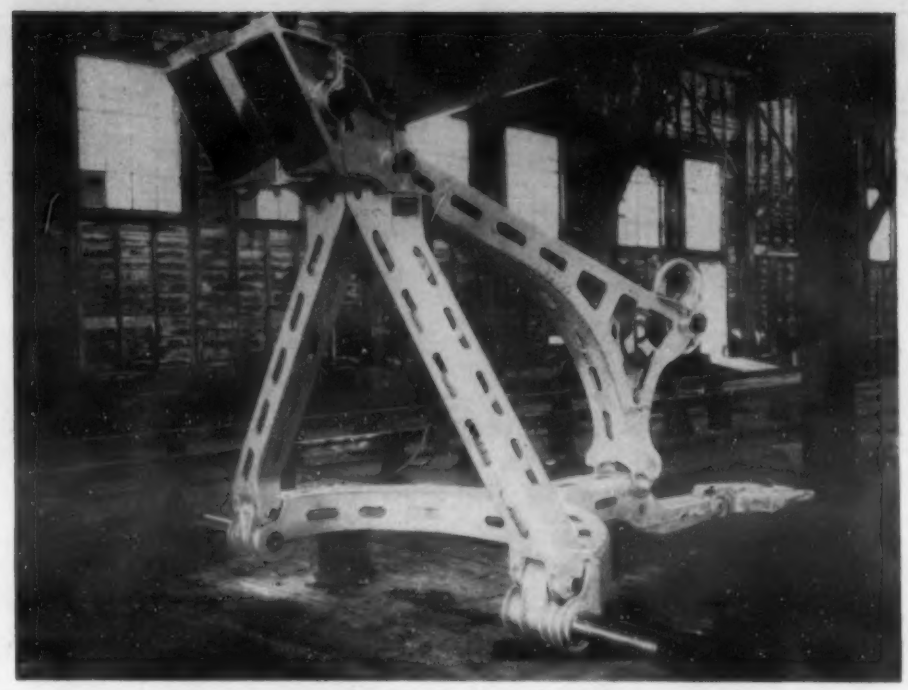


Fig. 6—Heavier Model of a Boom Yarder.

several of the component parts of this unit, more than 200 of which have been placed in service during the past 3 yrs. Fig. 3 shows a model of the boom yarder assembled except for wheels. The boom is a full box section as are all other members. Its finished weight is 950 lbs. and is 11 ft. 1½ in. overall in length with a maximum metal thickness of ½ in. The lower member, or reach, in the form of a wishbone, weighs 1655 lbs., has an overall length of 10 ft 2¼ in. and a metal thickness of ⅝ in. The two uprights, or struts, are 6 ft. 2 in. long and weigh 264 lbs. each. Like the boom, they have a wall thickness of ½ in. These castings are molded in green sand, gated at one end and poured through a single gate.

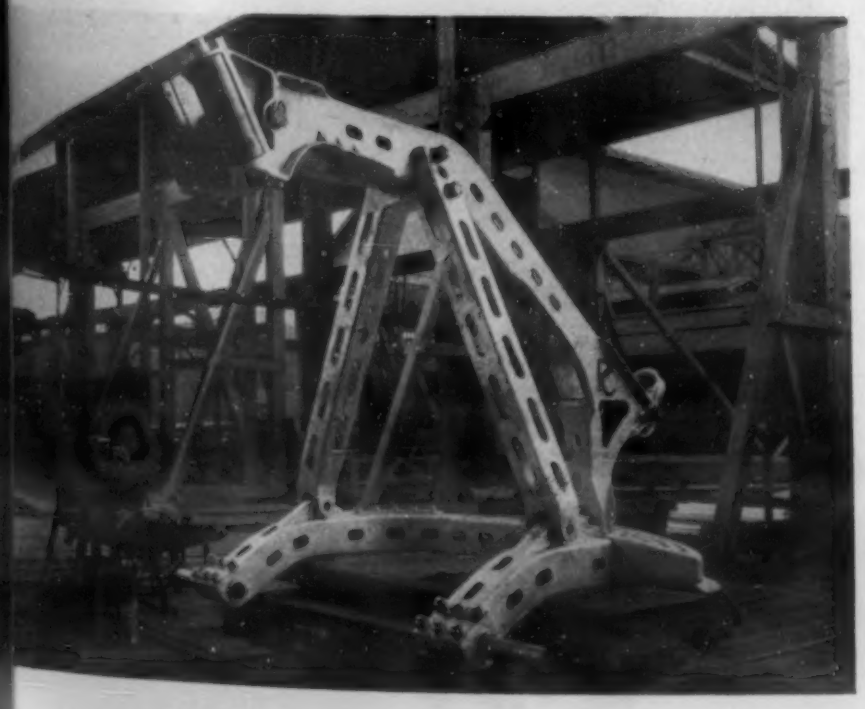
Figs. 6 and 7 are examples of heavier models of this machine. In the design shown in Fig. 7, the reader's notice is directed to the length of the boom which projects nearly 4 ft. beyond the fulcrum point and is severely stressed in service as a cantilever beam.

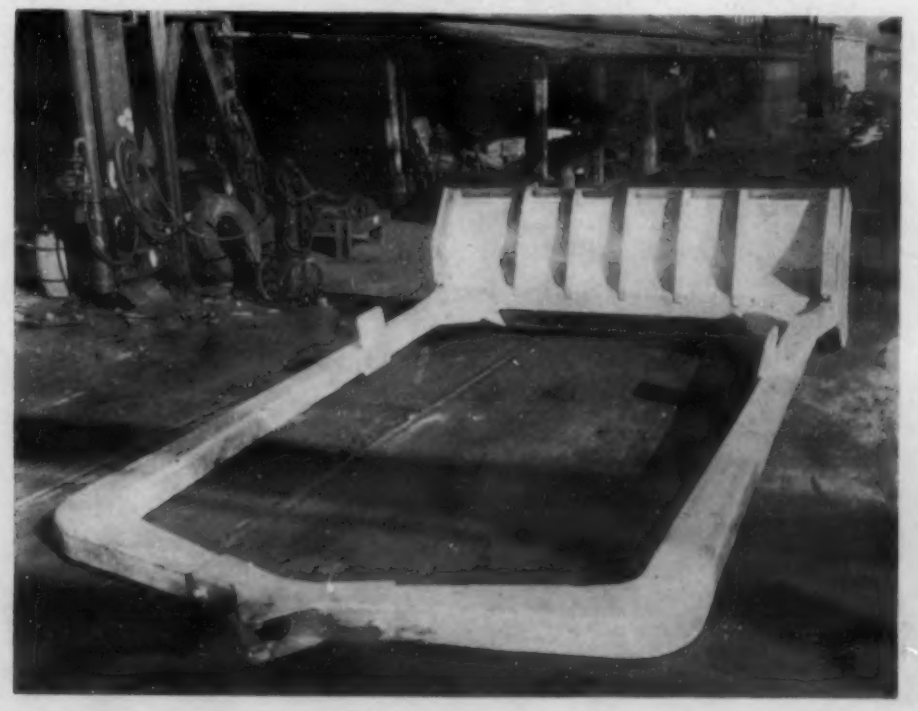
Carcometal is essentially a low carbon, copper-silicon steel containing about twice the usual amount of manganese. Its composition[1] and static tensile properties have been discussed at length by Gregg and Daniloff[2], while recent fatigue tests have disclosed an endurance ratio of 49 to 51 in the annealed condition. Its capacity to absorb kinetic energy as indicated by Izod and Charpy is unusually high, a value which is substantiated in a practical way by its resistance to repeated shock loading in the described applications. However, as it is desired to consider only the performance of castings made from this material rather than the chemical and metallurgical aspects of the alloy itself, we shall leave this as the subject of another discussion and refer again to the illustrations.

Other photographs reproduced show an extended application of the unique characteristics exhibited by Carcometal in the creation of castings involving a yet more unusual design than the foregoing though exposed to stresses of a more highly complicated nature. In Fig. 8 is pictured an assembled bulldozer frame for a Model "75" Diesel Caterpillar tractor. Another illustration, Fig. 9, shows how this unit is mounted and applied to roadbuilding service. The frame itself, without the moldboard, is made up of two main members joined together at the rear end by a third, or yoke casting. The L-shaped side castings have an axial length of 19½ ft. and are box section with a wall thick-

Fig. 7—Another Example of a Heavier Model Boom Yarder.

Fig. 8—An Assembled Bulldozer Frame for a Diesel Caterpillar Tractor.





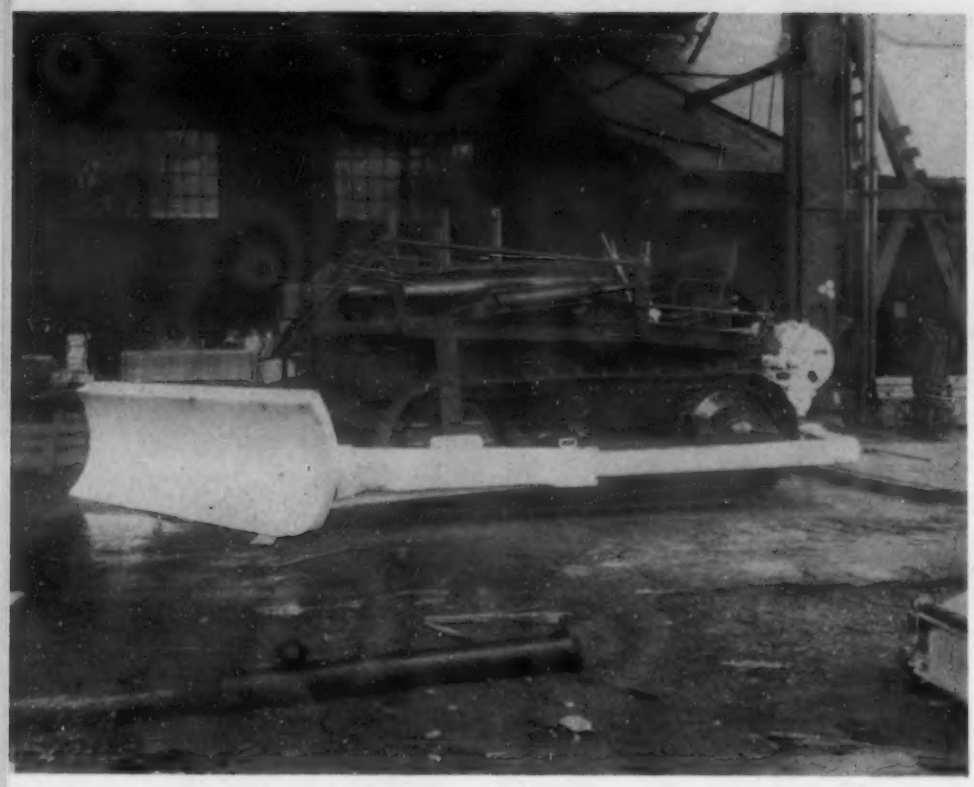


Fig. 9—The Bulldozer Frame Mounted for Application to Road Building Service.

ness of 5/8 in. As in the logging yarder, they are single piece castings, weighing 1226 lbs. and are poured from one end through a single gate, the metal being thus required to run the full distance of more than 20 ft.

Examples of still greater complexity both in design and foundry technique are displayed in other illustrations. Fig. 10 is the housing, or case, for a double drum geared hoist manufactured as adjunct equipment for the boom yarder logging unit, although frequently employed in individual service. The pouring of this casting at first presented some rather vexing problems, requiring ingenious correctives. Distortion and unequal shrinkage due to non-symmetry were the chief difficulties but adjustments in the pattern to compensate for inequalities, together with some changes in the methods of gating and core setting, resulted in perfect castings now on a routine production basis.

Fig. 11—The Housing, or Case, Fully Machined.

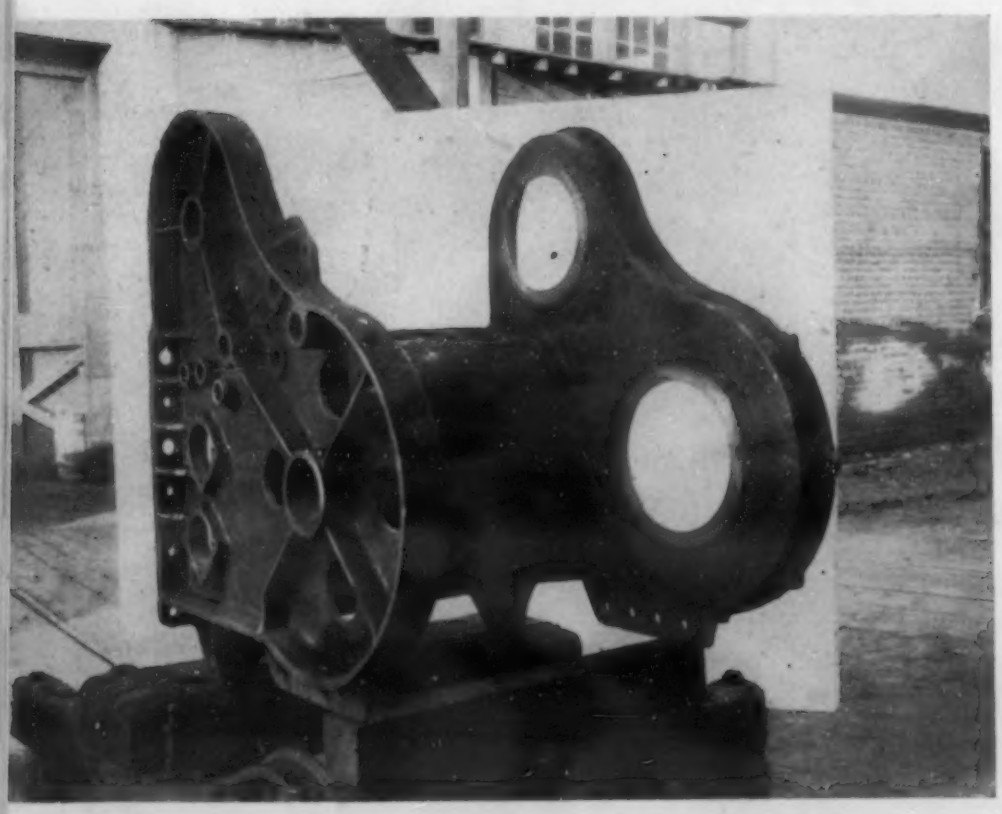
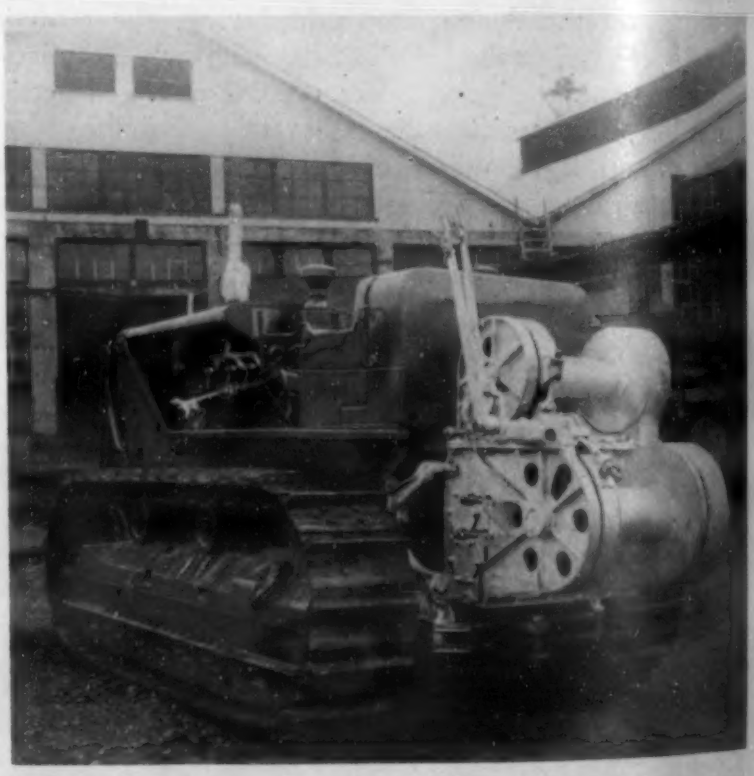


Fig. 10 shows two views of the case; one just as it is removed from the mold and one after having been cleaned and annealed. Fig. 11 shows the casting fully machined and ready for the assembly room. In Fig. 12 it is seen containing or supporting all the appurtenances of the completed hoist, and mounted for service. The general overall dimensions of this casting are especially interesting, for although representing a space volume of some 35 cu. ft. it weighs only 910 lbs., and has a maximum metal thickness of 7/16 in.

The next group of illustrations shows how a suitable type of low alloy cast steel may be applied in a field for-

Fig. 10—A Housing, or Case, for a Double Geared Hoist.

Fig. 12—The Housing, or Case, Supporting All the Appurtenances for the Completed Hoist.



merly regarded, both by right of competence and engineering tradition, as the exclusive territory of wrought structural assemblies mechanically joined. The castings pictured in this group are beyond question associated with the most rigorous kind of service and, although they replace members which have an average life varying from only a few weeks to a few months, no failure of any nature has ever been reported in the cast structures even after having been

in use for several years. The illustrations show how low alloy steel castings are extended to the main, and most severely stressed members, of excavating machinery. Fig. 13 is a 28-ft. steam shovel boom as it appears immediately upon shaking from the mold. It is made in a box section and has a finished weight of 4400 lbs. Its greatest width is 17¾ in. and greatest depth 26 in. Fig. 14 is another view

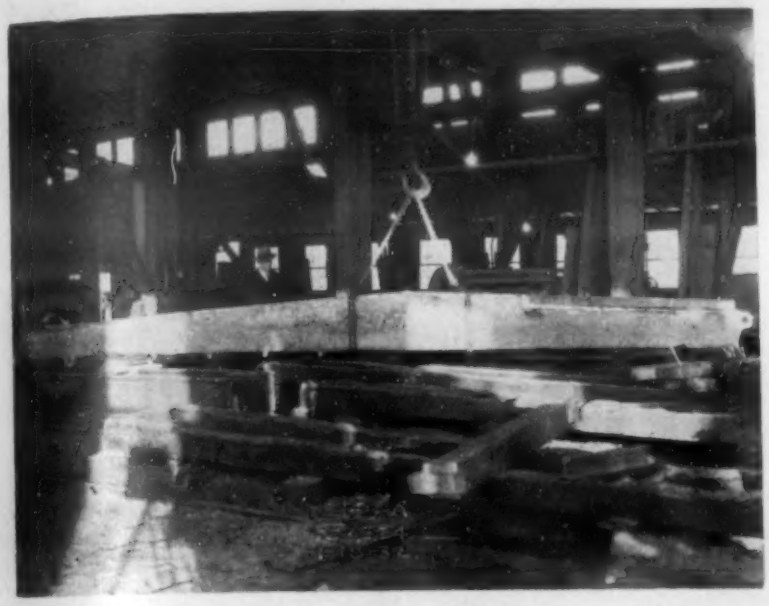


Fig. 13—A 28-Ft. Steam Shovel Boom As It Appears After Shaking from the Mold.

Fig. 15—Another Type of Boom Used on a Speeder Shovel.

of this boom finished and mounted with sheaves and saddle. Fig. 15 is another type of boom used on a speeder shovel. It has a total length of 19 ft. and weighs about 2100 lbs. Dipper sticks for these booms are made in various sizes for shovels of all capacities. These sticks are 5 in. x 12 in. x 19 ft., full box section with ⅞ in. metal thickness on all sides.

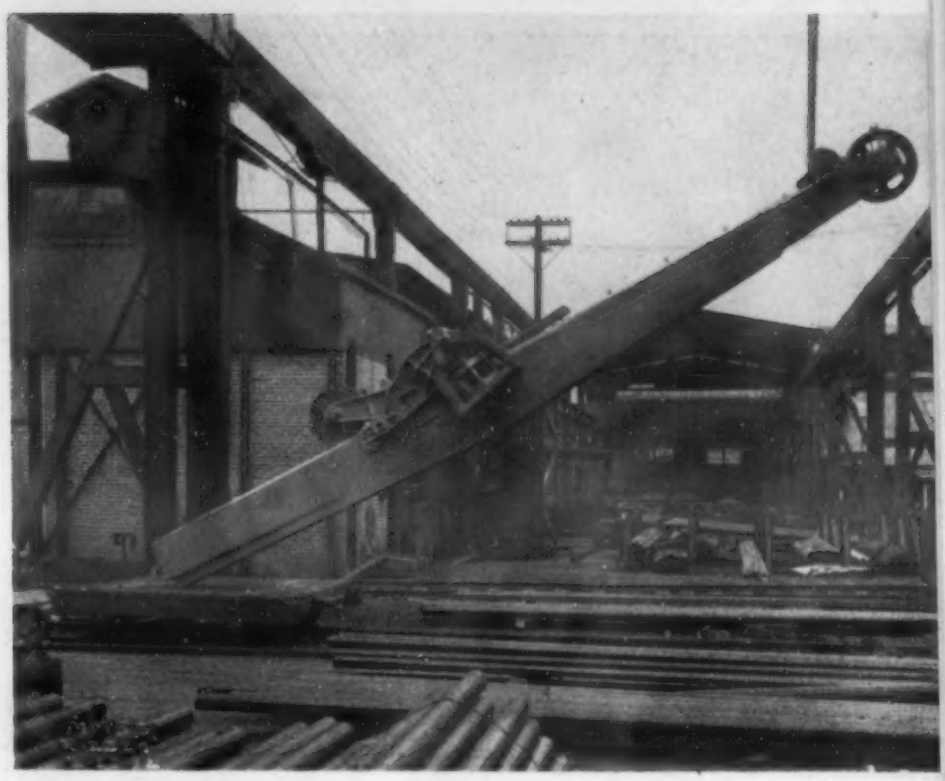
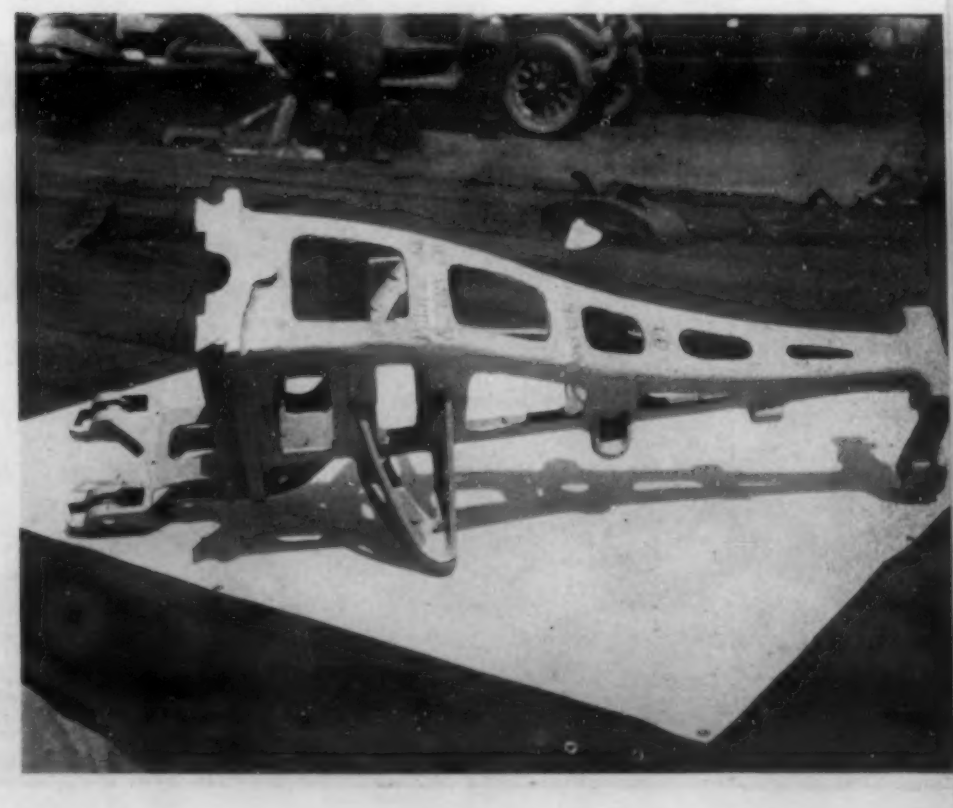


Fig. 14—Another View of the Boom, Finished and Mounted.

To indicate the extreme flexibility of this alloy in pouring either very light or very heavy sections, a small machine frame is shown in Fig. 16 and a heavy shafting in Fig. 17. The former is for a wood gainer used in shaping car sills, and supports two motors driving knives at high speed. It is about 3 ft. long, cast in one piece with ¼ in. metal thickness and weighs 45 lbs. in the rough. The latter, Fig. 17, is a shaft for a 20-ton Norton stone used in a pulp mill. It has a rough weight of more than 6000 lbs. The length is 15 ft. and the greatest diameter 14 in. For a 10-ft. shaft rough turned, the greatest diameter is 11¼ in. and the finished weight 2580 lbs.

Another unusual casting is the tie tram frame or cradle seen in Figs. 18 and 19. It is used in a Rueping tank for creosoting ties and although not severely stressed is exposed to warping and corrosion, to both of which condi-

Fig. 16—A Small Machine Frame of Low Alloy Cast Steel.



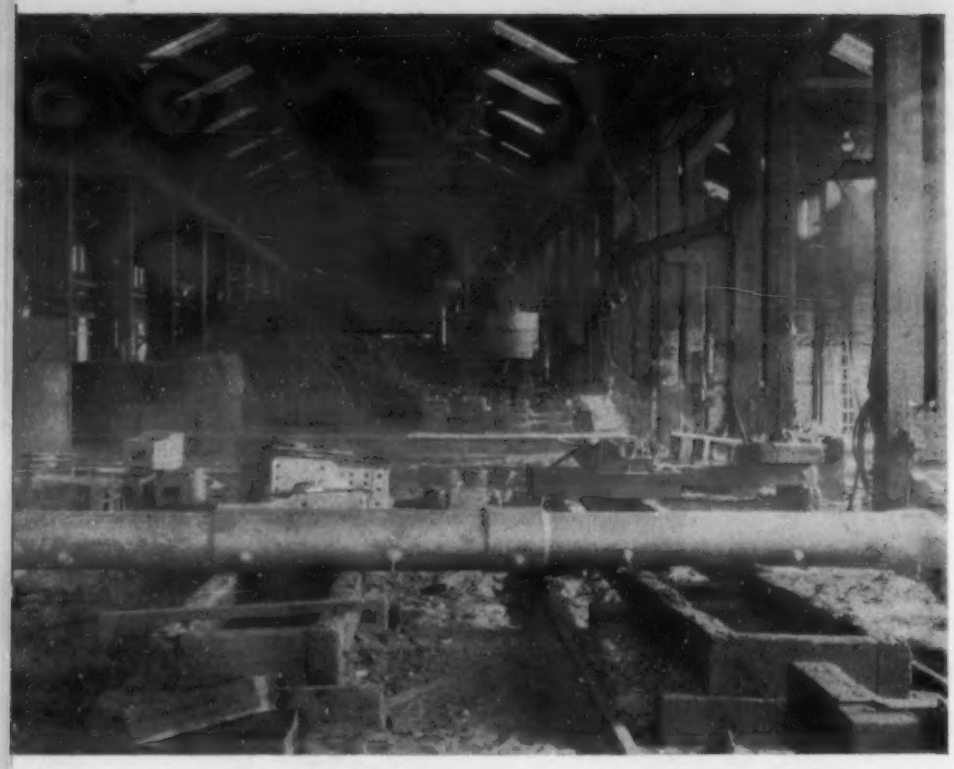


Fig. 17—A Heavy Shafting of Low Alloy Cast Steel.

tions the alloy manifests much greater resistance than the ordinary steels of commerce.

While it would be possible to present examples such as these to the point of weariness the foregoing have been selected as typical of the various departments of engineering service in which low alloy steel castings are not only entirely adequate but unique and self-contained to a degree not possible in any other type of construction.

The melting and pouring characteristics of the alloy used in the production of these castings lend themselves especially to the running of long, thin members as exhibited by the test sections illustrated in Fig. 20. In this respect it much resembles cast iron, and the shortened cooling time of thinner sections becomes a considerable factor in reducing the period to which the sand is exposed to the burning action of the molten steel, resulting in cleaner, smoother surfaces. The lower melting point of the alloy, significantly less than that of ordinary carbon steel, also

Fig. 18—The Tie Frame or Cradle is Another Unusual Casting.

aids in this respect, and as it thus manifests less shrinkage, there is less tendency to hot tears or cooling cracks.

Such castings as we have here described, although representing in themselves a definite advance in the steel foundryman's art, are but the forerunner of much greater accomplishments which may be expected from this industry in the near future. In the meantime, with high strength cast steel available to the designer, definite financial and mechanical economies are indicated by the use of castings,

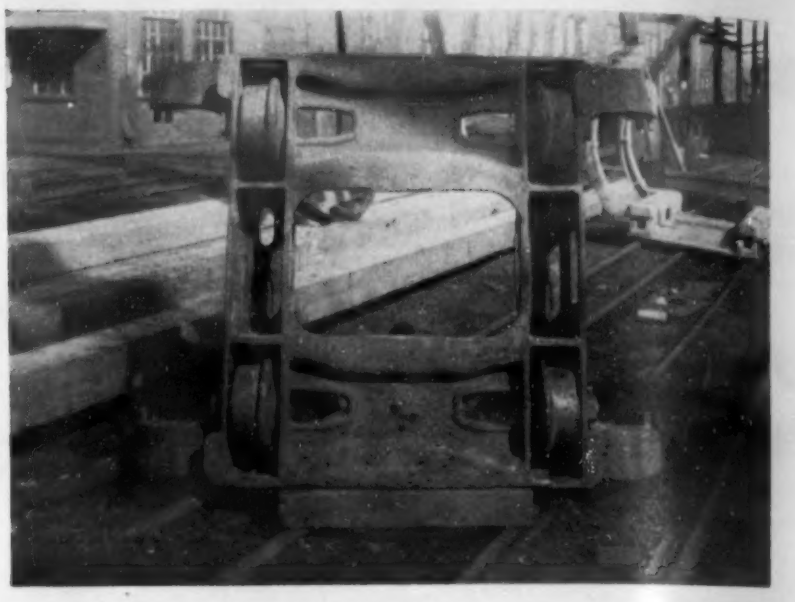
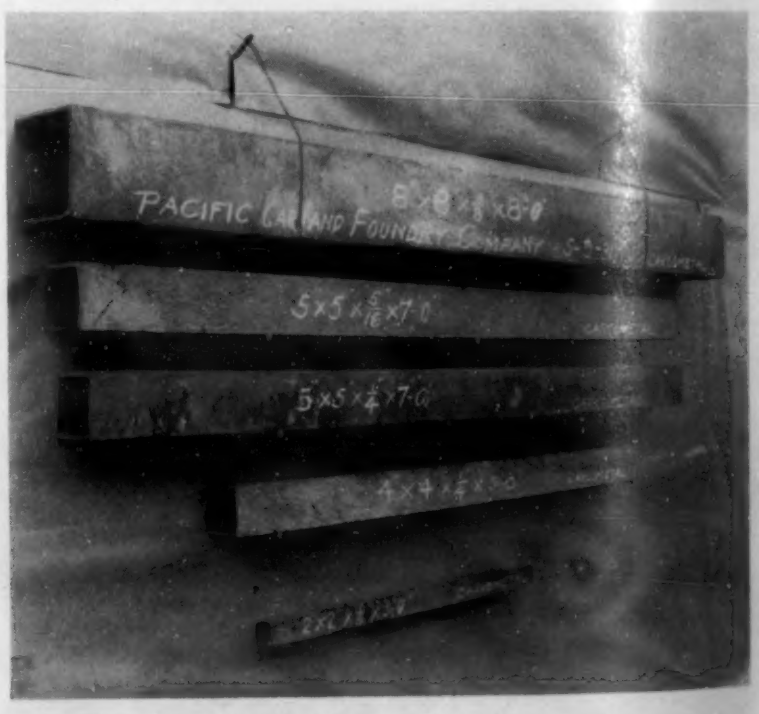


Fig. 19—The Tie Frame Assembled in a Cradle Car.

Fig. 20—Thin Members Which Have Been Cast with the Low Alloy Steel.



particularly where quantities of any magnitude are required from one design.

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[1] U. S. Patent No. 2,034,136, issued March 17, 1936.

[2] "The Alloys of Iron and Copper." McGraw-Hill Book Co., New York, 1934. [One example quoted by Gregg and Daniloff gives a composition of 0.11% C, 1.04% Mn, 1.23% Si, 1.74% Cu, which showed the following properties:

	Tensile Strength	Yield Point	Elong.	R. A.
Annealed at 1740 deg. F..	81,500	64,000	31	56
Annealed at 1740 deg. F., normalized at 1580 deg., precipitation hardened at 915 deg.	106,500	88,500	25	53

Editor.]

MECHANICAL PROPERTIES OF

Four Binary Tin Bronzes—II

AT ROOM AND ELEVATED TEMPERATURES

Concluded from the August Issue

by Claus G. Goetzel

Metallurgist, Hardy Metallurgical Co., New York

The results of metallographic tests are shown in Figs. 6-17. All structures except the 80/20 alloy could be homogenized with this annealing procedure.

With the 94/6 and 90/10 alloys, a different appearance of the specimen surface could be seen on the ruptured test pieces after tests at room temperature. These differences were independent of the type of the material, (i.e. whether cast or annealed). Figs. 18 and 19 show a variety of broken specimens, on which one can plainly see that some of the surfaces are finely wrinkled and some coarsely wrinkled. Metallographic tests, on the other hand, showed for the same alloy two different grain sizes (Figs. 6, 7, 9 and 10) which also did not depend on the type of the material. Metallographic tests on cut-off heads of cast and annealed tension test pieces of the 90/10 alloy with different surfaces confirmed the supposition of a connection between the various grain sizes and surfaces of the specimens (Fig. 20). The grain structures of the heads cut off from the specimens with coarsely wrinkled surfaces show large grains and the grain structures of specimens with finely wrinkled surfaces show small grains, all of this being independent of the type of material. The sketches in Fig. 21 give a review of the position of the various test pieces and Brinell samples in the three castings of the alloy Cu-Sn 90/10; this plainly shows that there is a relation between the different surfaces and grain sizes of the specimens, and that they manifest themselves independently of the type (cast or annealed) and of their position in the casting molds. Regarding the tensile properties, the fine grained, finely wrinkled specimens showed no considerable differences versus the coarsely grained, coarsely wrinkled samples. The fractures of specimens made from the 94/6 alloy at the six different temperatures are shown in Fig. 22. At 20 deg. C. the structure of the fracture was very fine but became coarser up to 200 deg. C. At 300 and 400 deg. C.

Fig. 6.—Grain Structure of the Cu-Sn 94/6 Alloy (Annealed Type), Etched With CrO_3 + H_2SO_4. Magnification 300 X.

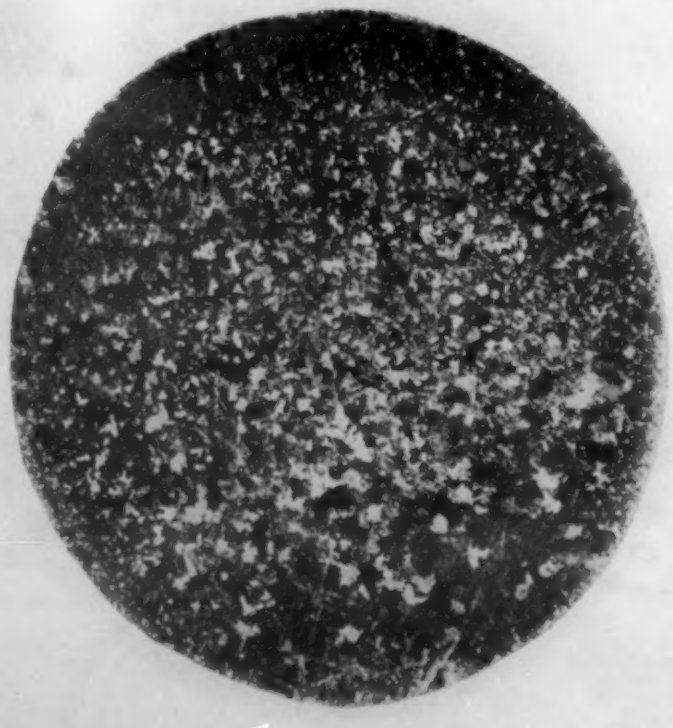

Fig. 7.—Grain Structure of the Cu-Sn 94/6 Alloy (Annealed Type), Etched With CrO_3 + H_2SO_4. Magnification 3 X.

Fig. 8.—Grain Structure of the Cu-Sn 90/10 Alloy (Annealed Type) Etched With $FeCl_3$. Magnification 80 X.

Fig. 9.—Grain Structure of the Cu-Sn 90/10 Alloy (Cast Type), Etched With $CrO_3 + H_2SO_4$. Magnification 3 X.

the fracture was intergranular, while at 500 deg. C., the structure was burnt.

Critical Analysis of the Test Results

The foregoing series of investigations offers not only a comparison of the properties of each of the separate alloys in the cast as against the annealed form at room and at elevated temperatures, but also a comparison of the various alloys with each other.

The rolling bronze Cu-Sn 94/6 at room and at elevated temperatures reveals no practical important difference between the cast and the annealed material. The cast 90/10 bronze behaved similarly. Cast 86/14, however, in distinct contrast to this, has lower tensile strength and elongation values in the cast type at room temperature. The values for the yield points, for the modulus of elasticity and for the Brinell hardness at room temperature are higher than the values in the annealed type. With rising temperatures, the physical properties, for both cast and annealed materials, decrease in value, with the exceptions of the elongation and reduction of area values in the cast type. An occasional overlapping of values is considered of no practical significance. The 80/20 alloy shows no difference of practical importance between the cast and the annealed types at room and at elevated temperatures.

As a result of these investigations one can state that, under prevailing favorable thermal conditions in the process of solidification and of cooling of the 94/6 and 90/10 alloys, one has already obtained a type of grain structure which, to the greatest possible extent, approaches the ideal homogeneous state, at least in accordance with the earlier type of copper-tin diagram. Evidently it is a different matter with the alloys similar to cast 86/14 bronze, where

Fig. 10.—Grain Structure of the Cu-Sn 90/10 Alloy (Cast Type), Etched With $CrO_3 + H_2SO_4$. Magnification 3 X.

Fig. 11.—Grain Structure of the Cu-Sn 86/14 Alloy (Annealed Type), Etched With $FeCl_3$. Magnification 80 X.

Fig. 12.—Grain Structure of the Cu-Sn 86/14 Alloy (Cast Type), Etched With $FeCl_3$. Magnification 80 X.

the existing number of crystals resulting from solidification and cooling seem to be too great to be balanced during these processes, so that a subsequent compensating anneal must have an important effect. Again, in the case of the 80/20 alloy, the normal amount of brittle grains (according to the earlier diagram, *δ-crystals*, and according to the later diagram, *grains* of the compound Cu_3Sn,) is so great that a compensating anneal can hardly influence the mechanical properties typical of this casting alloy. The relative lack of response of all but the alloy Cu-Sn 86/14 to annealing is of some importance. (The variation from results of previous investigations on this line may be explained as follows:—in our case the material was not deformed prior to annealing, whereas in the investigation of Rawdon, for instance, differences were found between the cast material and an annealed material, which was cold worked before the heat treatment). If one combines the

Fig. 14.—Grain Structure of the Cu-Sn 80/20 Alloy (Cast Type), Etched With Copper-Ammonium-Chloride. Magnification 80 X.

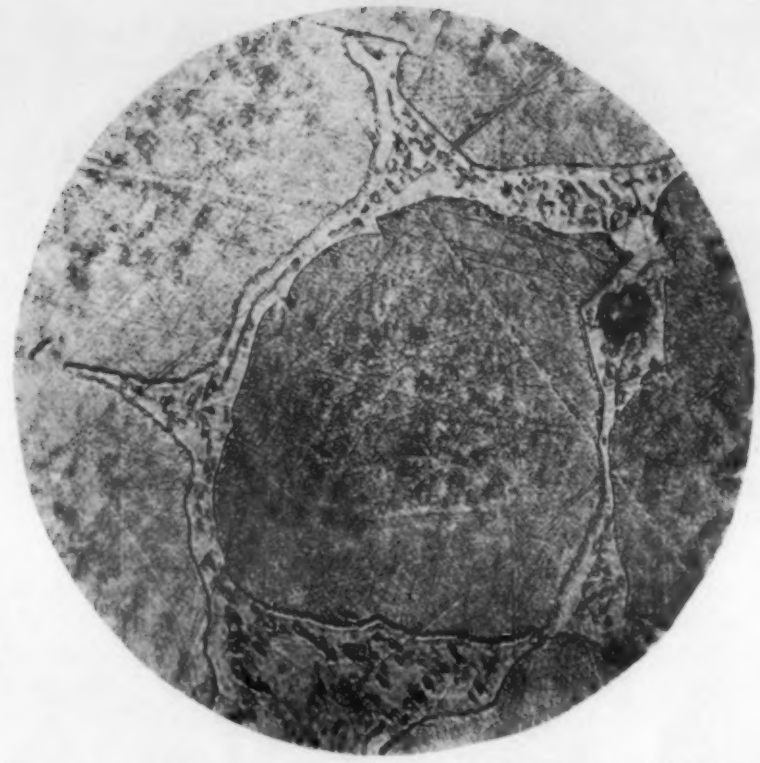

Fig. 13.—Grain Structure of the Cu-Sn 86/14 Alloy (Cast Type), Etched With $FeCl_3$. Magnification 500 X.

alloys tested in groups, 2 different but related groups result, namely:

(1)		(2)	
94/6	Cast	86/14	Cast
94/6	Annealed	80/20	Cast
90/10	Cast	80/20	Annealed
90/10	Annealed		
86/14	Annealed		

among which the alloy Cu-Sn 86/14 has a position in the middle.

Table V. Comparison of Cast Alloys Tested with German Standard Bronzes.

	GBz 10 Cu-Sn 90/10		GBz 14 Cu-Sn 86/14		GBz 20 Cu-Sn 80/20	
	Author	Standard	Author	Standard	Author	Standard
Tensile Strength, lbs. per sq. in.	45,515	28,446	32,714	28,446	27,024	21,335
Elongation, per cent	45	15	7	3	0	0
Brinell hardness.	62	60	79	90	120	180

Fig. 15.—Grain Structure of the Cu-Sn 80/20 Alloy (Cast Type), Etched With $FeCl_3$. Magnification 500 X.

Fig. 16.—Grain Structure of the 80/20 Cu-Sn Alloy (Annealed Type), Etched With Copper-Ammonium-Chloride. Magnification 80 X.

Fig. 17—Grain Structure of the 80/20 Cu-Sn Alloy (Annealed Type), Etched With $FeCl_3$. Magnification 500 X.

The characteristic properties of the cast and the annealed specimens of the tested alloys, such as the 0.2 per cent yield strength, the tensile strength, the elongation and the Brinell hardness should be compared at room temperature, because they are the properties ordinarily recorded. From and annealed), 90/10 (cast and annealed) and 86/14 (annealed) alloys with one another, on one hand, and Table III one can clearly see that comparing the 94/6 (cast comparing the 86/14 (cast) and 80/20 (cast and annealed) alloys with each other, on the other hand reveals no important differences between the two types of material. The exception is the Brinell hardness.

One must clarify the situation concerning the actual performance of the alloys investigated in this research work —of course in the cast type only—in comparison with common data obtainable in the industries, of which the German Industrial Standards might give an average (Table IV). In comparison with the American Standard values for the alloy B 60 (Cu-Sn-Zn 88/10/2), which would approximately correspond to the binary alloy Cu-Sn 90/10, the tensile strength of the binary alloy was approximately 20 per cent higher, the yield strength also about 20 per cent higher and the elongation approximately 100 per cent higher. In connection with this, however, it should be stated that the binary alloys in question were simple sand mold castings which, when produced, were carefully heat treated so that maximum values for the physical properties could be obtained. Consequently this means that, if other materials are used for the molds, one has to expect a change in the above-mentioned properties, especially when considering the so-called "reversed ingot segregation" of the bronzes. Furthermore the castings were produced by a simple casting method. It is a matter of course that the mentioned properties may experience changes in their values if other casting methods are used. Besides this the investigated alloys were made from virgin materials. If other original raw materials are used, one must naturally expect a corresponding change in the values of the physical properties.

The above investigations have shown that with expert

Fig. 18.—Variety of Broken Tensile Specimens of the Cu-Sn 94/6 Alloy (Cast Type) With a Different Surface Appearance.

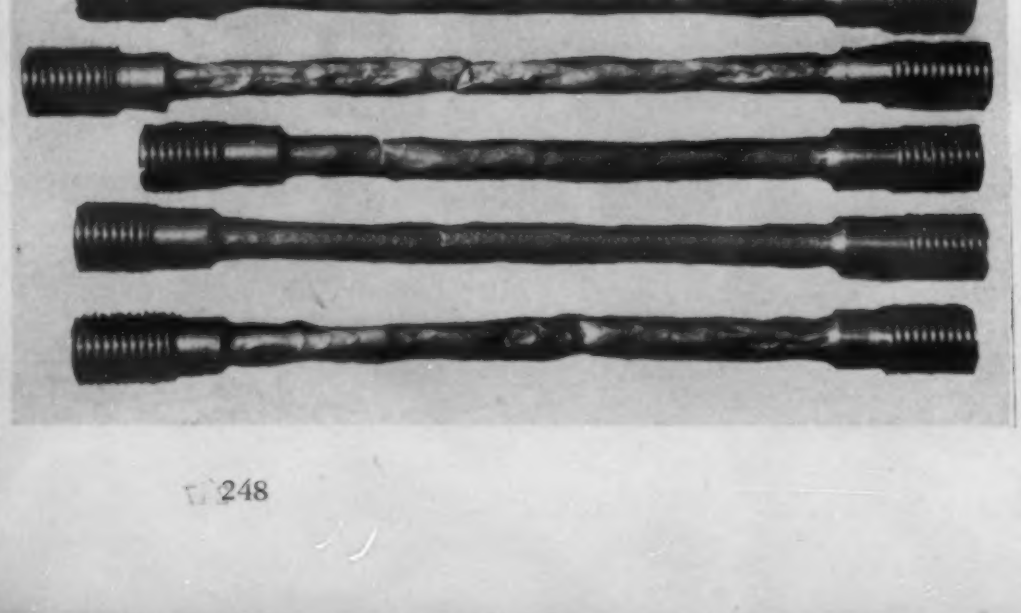

Fig. 19.—Variety of Broken Tensile Specimens of the Cu-Sn 90/10 Alloy (Cast and Annealed Types). Specimen numbers, from left to right, are 26, 27, 37, 39 and 46.

casting technique one can obtain maximum values of the mechanical properties of the cast binary tin bronzes, which at the present are not generally obtainable. They served also to determine the physical properties of the tin bronzes Cu-Sn 94/6, 90/10, 86/14 and 80/20 in the cast and in the annealed form at elevated temperatures (Table IV). From these values we may conclude that the binary tin bronzes of the cast type can be stressed for short times without danger up to temperatures of 200 to 300 deg. C.

Inasmuch as the investigations were made only as short time tension tests, at high temperatures (according to the classification of the A.S.T.M.) the results cannot be interpreted as any indication of relative "creep" strengths; the "creep" effect must be clarified by special long time tension tests at high temperatures.

Acknowledgment

The above investigations were made at the Institut für angewandte Metallkunde of the Technische Hochschule, Charlottenburg, Berlin, Germany (Prof. Dr. W. Guertler). For the foundry work, the plants of the Deutsche Werke, A.G., Berlin-Spandau were placed at our disposal. The main part of the mechanical testing was done at the "Staatliches Materialprüfungsamt", Berlin-Dahlem, Germany.

The writer wishes to acknowledge his indebtedness to the following for their kind assistance and advice: Dr. W. Claus for theoretical preparation and exploration of the research work, Prof. Dr. W. Guertler, Berlin, and the gentlemen of the "Deutsche Forschungsgemeinschaft", Berlin, for facilities and general advice.

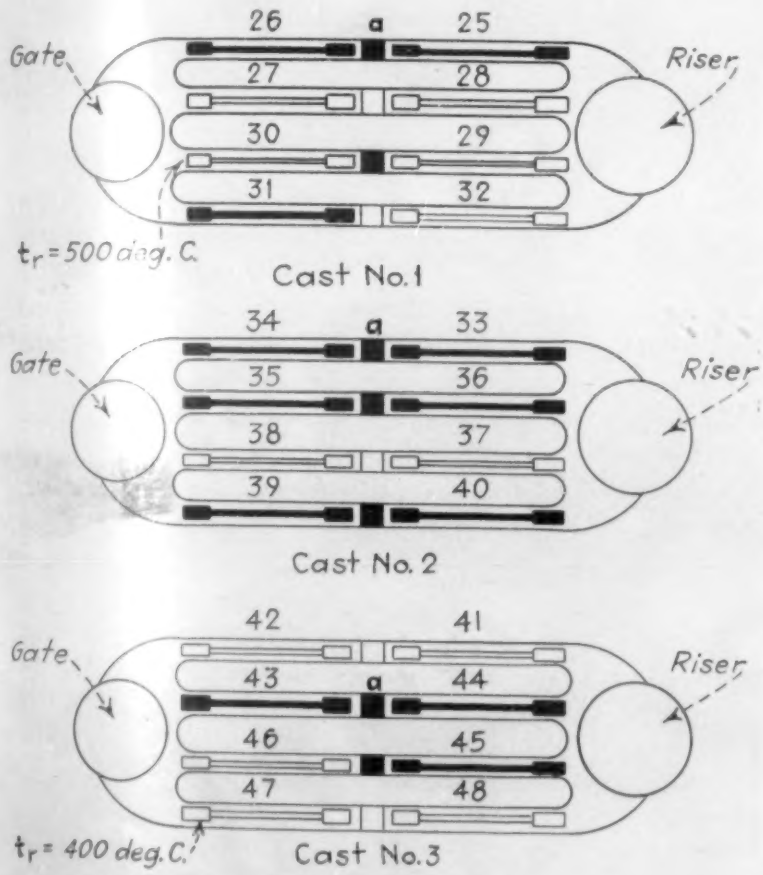

Fig. 21.—Position of Test Pieces in the Three Castings of the Cu-Sn 90/10 Alloy.

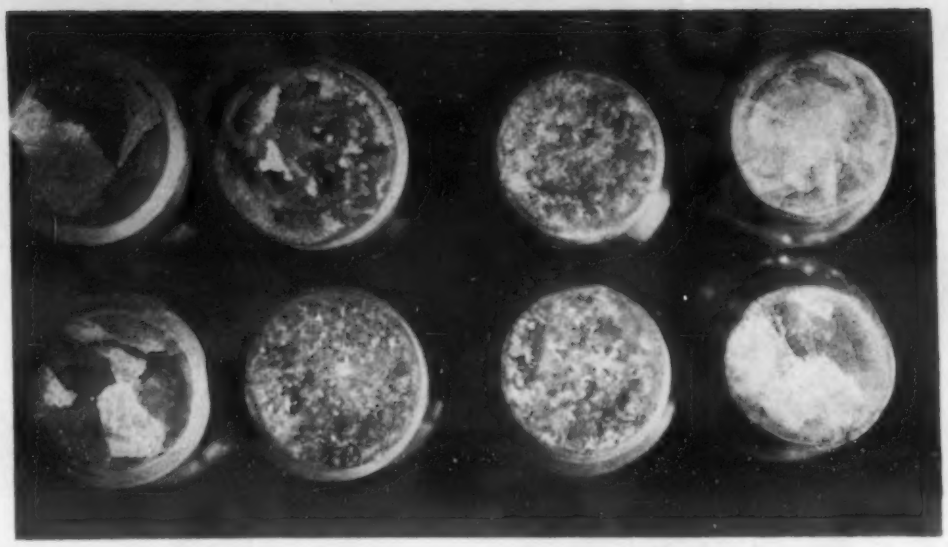

Fig. 20.—Grain Structures of Cut-off Heads of Cast and Annealed Tension Specimens of Alloys Cu-Sn 94/6, and Cu-Sn 90/10. The four samples on the left are 94/6, on the right 90/10; top row are cast samples, bottom annealed.

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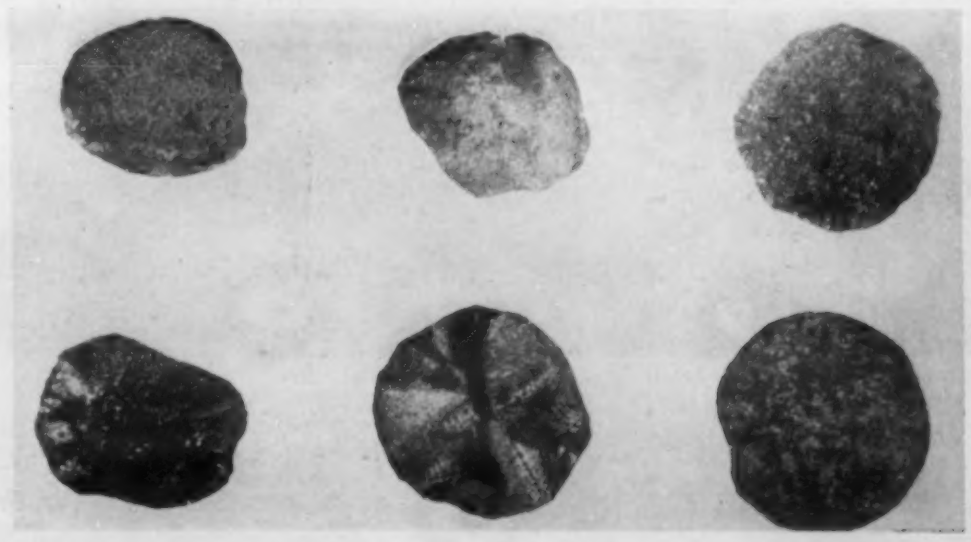
Fig. 22.—Fractures of Tensile Specimens of the Annealed Cu-Sn 94/6 Alloy Tested at Different Temperatures. From left to right, top: 20, 100 and 200 deg. C.; bottom: 300, 400 and 500 deg. C.



Courtesy: Carnegie-Illinois Steel Corp.

Ingot of Steel Being Lifted from Soaking Pits after It Has Been Heated to the Temperature Necessary for Subsequently Rolling into Rails.

A CORRELATED ABSTRACT ON

SUPERLATTICES

by Charles S. Barrett

Metals Research Laboratory and Lecturer in the Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh

THERE HAVE BEEN FEW PERIODS in the history of physical metallurgy when the understanding of fundamental principles of metal structures has advanced as rapidly as it has of late, with so much attention being focused on superlattices by both physicists and metallurgists, and on the electron theory of metals by quantum mechanics experts. The task of explaining in ordinary words the recent developments in the latter field is difficult enough to make anyone pause, but the field of superlattices, on the contrary, is based on principles fundamentally so simple and reasonable as to make the reporter's task a pleasure.

A story of these developments in chronological order would be interesting reading, but the requirements of a correlated abstract can better be met by disregarding this order. By passing briefly over the controversies that have raged over ideas that have since turned out to be half-truths, it will be possible to have more space for reporting the phenomena as we now understand them.

The study of superlattices has brought out the answer to some puzzling metallurgical questions such as the nature of the transformation from β to β' brass, but it has done more than this. It has provided a remarkably clear view of the dynamic conditions inside of metallic crystals, the balance between the tendency of thermal agitation to produce a chaotic condition in the crystals, and the opposing tendency of interatomic forces to produce regularity. It has also shown the correlation between a wide range of alloy structures varying from ideal solid solutions at the one extreme to ideal compounds at the other, and has provided an understanding of certain complicated variations in the physical properties of some of these phases and of the effect of heat treatments.

It is frequently stated that Tammann[1] first suggested "ordering" in solid solutions and that Johansson and Linde[2] first proved it by X-rays in 1925. It is curious that the observations that led Tammann to postulate superlattices, namely "resistance limits"—the abrupt change in the resistance to acid attack of alloys of certain compositions, have since been explained in other ways and seem but little related to superlattices.[3] Much of the credit for discovering superlattices belongs rightfully to Bain, who was the first to find them in solid solutions by X-ray diffraction. In 1923 Bain[4] found "supernumerary lines" in his spectrograms of particularly well annealed alloys of Cu-Ni and Cu-Au that could not be accounted for by the face-centered lattice of the ordinary solid solution, but that indicated a segregation of atoms to particular lattice points, and a resultant altering of the periodicity of the lattice. Bain not only proposed the correct explanation for these lines, but he stated at what compositions they would, in general, be

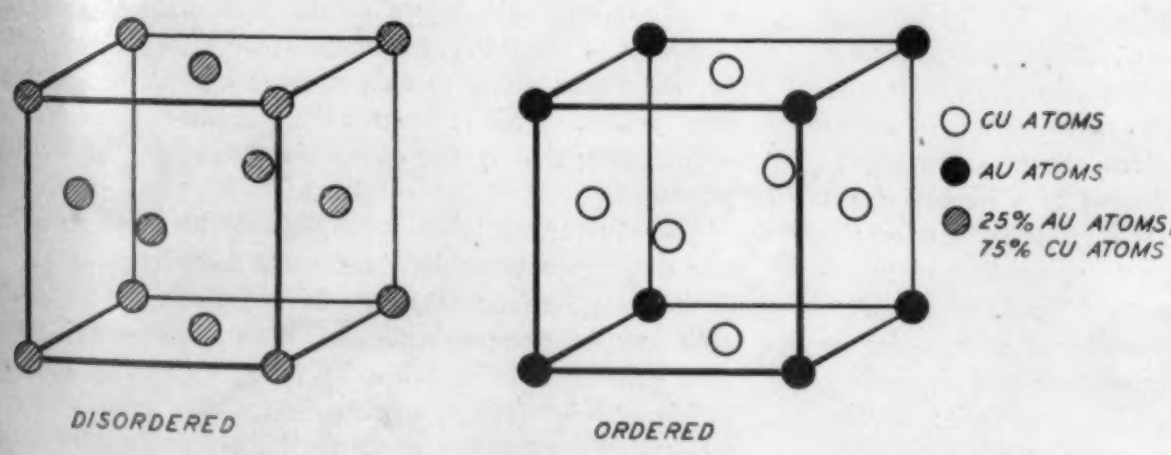


Fig. 1 a and b.The superlattice $AuCu_3$ (cubic).

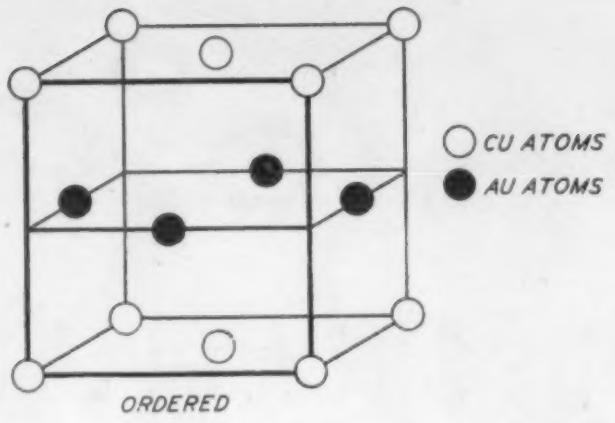


Fig. 2. The superlattice AuCu (tetragonal).

apt to occur, and explained that in certain alloys the X-ray method of investigating them would run into difficulties; namely, when the different kinds of atoms in an alloy had similar reflecting power for the X-rays.

The Meaning of "Superlattice"

If atoms of two kinds arrange themselves on the points of a space lattice in a random way, each atom taking its position on one of the points without regard to the kinds of atoms on the neighboring points, they form a substitutional solid solution of the normal type. Many cases have now been discovered, however, where this random, disordered array may be changed by suitable annealing or slow cooling into an ordered array, in which atoms of one kind tend to segregate into a particular set of the atomic positions. The crystals are then known as "superlattices" ("superstructures," "Überstrukturen").

A definition of wider scope[5] states that either a substitutional or an interstitial solid solution becomes a superlattice when one or more of the kinds of atoms segregate to individual atomic positions or lattice interstices in preference to others, increasing the unit cell or lowering the symmetry, but causing little or no deformation of the lattice.

Is the superlattice transformation a change of phase? This is a question that has started countless arguments, but the answer now appears quite definitely, "No." It is no more logical to call β' brass a phase distinct from β than it is to call β iron a phase distinct from α iron. Let us consider first an alloy of equal numbers of two kinds of atoms that undergoes this transformation. Such an alloy in equilibrium at any temperature consists of a homogeneous single phase in which the atoms are changing places on the lattice points by thermal motion, yet are tending to segregate into the ordered arrangement. At each temperature the alloy ultimately becomes homogeneous with a degree of order characteristic of that temperature and depending on the balance of these two opposing tendencies; an infinitesimal increase in temperature never causes more than an infinitesimal increase in disorder. There is obviously no phase change in such a transformation (unless one considers it as a series of transformations between an infinite number of infinitesimally differing phases), and it should not be indicated on the phase diagram by lines that conform to the phase rule. In the case of compositions like AB_3, or any composition other than AB, theory indicates that at the critical temperature the order drops suddenly to zero from a finite value, and the transformation is accompanied by a latent heat. Theory indicates, however, that the partially ordered and the fully disordered lattices cannot coexist in equilibrium over a range of temperature or composition. This shows that the ordered and disordered conditions are not different phases and that the transformation is not a phase change, for if such were the case the phase rule would demand the existence of a two-phase region of finite range of temperature.

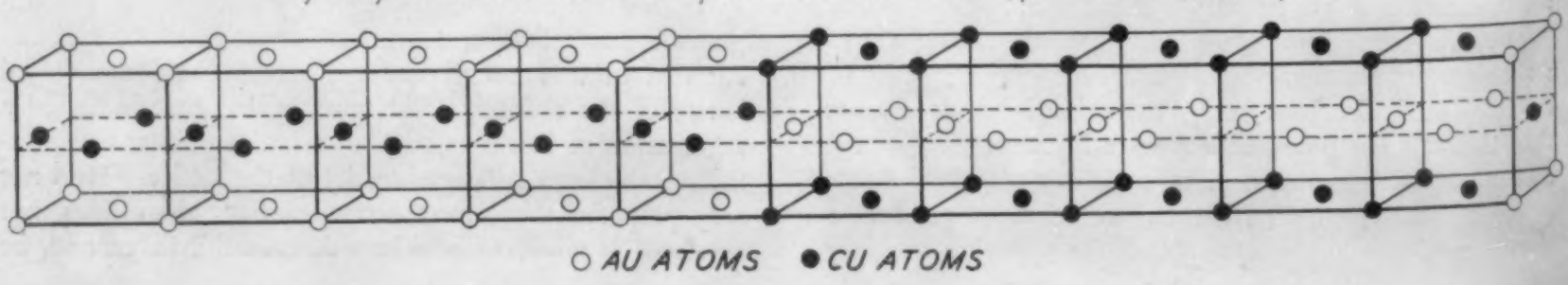
It must be admitted that the above discussion is based on the theoretical point of view. This may be defended by pointing out that the quesion cannot be answered definitely in the laboratory, for experiments can only show that if there is a two-phase region, it has a spread that is less than the magnitude of the experimental error (temperature gradients, etc.), and experiments can never prove its complete absence. Bragg and Williams[6] have put the matter very simply, from the crystallographer's point of view, by stating that the crystalline structure of a phase that distinguishes it from the other phases of the same alloy system is really a lattice of atomic sites, and the distribution of atoms on these sites may be varied (a superlattice appear, or the composition vary) without destroying the crystalline structure characteristic of the phase.

Typical Superlattices

Among the first alloys in which a transition from the disordered to the ordered state was proved are the copper-gold alloys containing in the neighborhood of 25 atomic per cent gold ($AuCu_3$).[2, 7, 8] The high temperature, disordered state of this alloy is a random array of Au and Cu atoms on a face-centered cubic lattice, Fig. 1a, but if the alloy is annealed below a critical temperature, about 400 deg. C. (750 deg. F.), the atoms segregate as shown in Fig. *1b*, Au atoms going to cube corners and Cu atoms to the face centers. This represents the condition when ordering is complete; that is, the equilibrium condition at low temperatures.

The Au-Cu alloys of approximately 50 atomic per cent also undergo a transformation from disorder to order, but in this case the face-centered cubic solid solution transforms with low temperature annealing to a face-centered tetragonal structure, AuCu, with the atoms segregated as shown in Fig. 2.[2, 7, 8] The term superlattice also applies to cases such as this, even though a small distortion of the lattice

Fig. 3. A superlattice recently found in AuCu (orthorhombic). The figure shows one unit cell, which is as long as ten of the face-centered cubic cells of the disordered state. (Johansson and Linde).



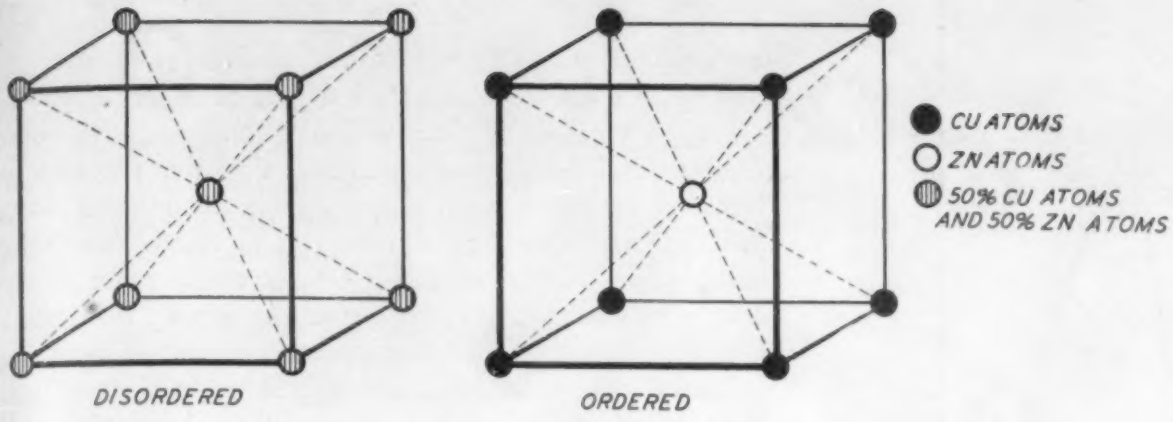


Fig. 4 a and b. The superlattice of β brass (CsCl type).

accompanies the appearance of order (the axial ratio c/a is about 0.94-0.95).

Frequently the type of ordering is such that the periodic repetition of the pattern is on a much larger scale and requires a unit cell several times larger than normal to describe it. The most striking example of this is the superlattice recently found by Johansson and Linde[8] in Au-Cu alloys of 47 to 53 atomic per cent annealed at 420 deg. C. (788 deg. F.). The unit cell, shown in Fig. 3, is orthorhombic; two edges of the cell are nearly equal, but the third is ten times as long. It is made up of a row of ten of the cells of the solid solution from which it formed. Another example that has been very carefully worked out, one that requires a unit cell embracing eight of the pre-existing cells, is found in the terminal solid solution of Al in Fe between 18 and 40 atomic per cent Al, the structure Fe_3Al.[9, 10] Beyond 40 and up to 50 atomic per cent in the Fe-Al system a superlattice is found that requires only a normal cell of the CsCl type for its description (Fig. 4).[9, 10, 11, 12, 13]

There is no need to list here all the superlattices that have been found. The list is constantly growing, and there are always a number that are uncertain. It should be stated, however, that the majority are of the simple types pictured in Figs. 1 and 4 and occur at compositions AB and AB_3, including the following,[14, 5] CuPd, CuBe, CuZn (β brass), AgMg, AgZn, AgCd, AuNi, NiAl, FeCo, all with the CsCl structure of Fig. 4, and $AuCu_3$, $PtCu_3$ $PdCu_3$, $FeNi_3$, $MnNi_3$, $(MnFe)Ni_3$ with the structure of Fig. 1; in close-packed hexagonal lattices of $MgCd_3$ and Mg_3Cd there is ordering without change of symmetry. In some cases the symmetry is altered upon superlattice formation.

An example is found in the Cu-Pt system at 50 atomic per cent, where the face-centered cubic disordered state changes to rhombohedral as a result of segregation of atoms of the two kinds on alternate (111) planes of the cubic lattice. In the Cu-Pd system one of the ordered structures has the body-centered cubic CsCl structure although it forms from a face-centered cubic disordered state. In spite of this change of lattice, however, it is probably a superlattice transformation, since the physical properties vary with temperature in a way similar to typical superlatices, and since it can be shown that a relatively small adjustment of lattice dimensions is required in the transformation instead of an extensive rearrangement of atoms.[14, 63]

Methods of Investigation

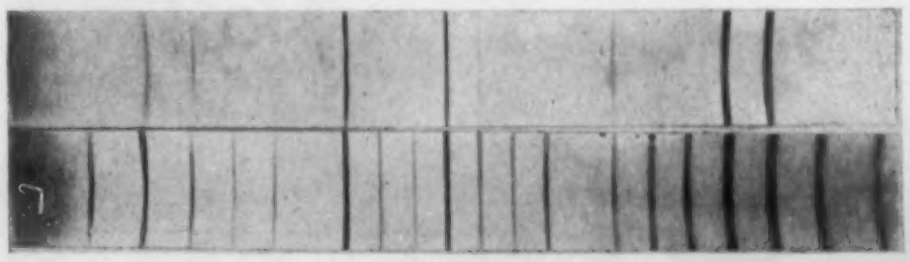
X-ray analysis of crystal structure has been beyond doubt the most effective tool in these researches, but almost all the other methods of investigation available to the physical metallurgist have contributed their share as well, and seldom has there been an example of more effective cooperation between different lines of theory and experiment. The atomic positions in the examples just cited, and in a considerable number of others, have been analyzed by their X-ray diffraction patterns, using the principle that when order begins to form out of disorder, certain new reflections will appear that have been suppressed in the disordered state as a result of destructive interference (see Fig. 5). These "superlattice lines" in the patterns have an intensity and breadth related to the degree of order in the alloy, but this relationship is not entirely simple and direct.

Ordered crystals may consist of regions within which there is consistent order, but the regions may not form a coherent pattern throughout the crystal, a condition which will affect the diffraction pattern. The X-ray method is therefore more or less insensitive to order if the order is uniform only in very minute nuclei scattered in a haphazard way throughout a crystal, but just how insensitive is a matter of dispute involving the applicability of particle size equations to the case.[8, 15, 16, 17] The method fails utterly, however, to analyze the atomic distribution in cases where the scattering power of the different kinds of atoms are equal, as they are in brass, and the distribution in β' (CuZn) must be deduced indirectly. (There is scarcely any doubt but that β' has the CsCl structure, however.)

Electrical resistance has been used in hundreds of investigations of this type. It reveals the degree of order in a way closely related to the X-ray method: It is insensitive to very small nuclei of "local" order and depends on order over relatively long distances, yet it detects the difference between order that extends coherently throughout the whole of a crystal and order coherent only in limited regions into which the crystal is partitioned.[16, 18] As an example of the resistivity of superlattices, some data on Au-Cu alloys are reproduced in Fig. 6.

Methods involving heat content and specific heat will detect both "local" and "long distance" order and therefore have been very useful in the development of superlattice theory.[19, 20, 21] The effective use of this thermal

Fig. 5. X-ray diffraction patterns from $AuCu_3$. (Sykes and Evans). Upper pattern from disordered alloy, lower from ordered alloy.



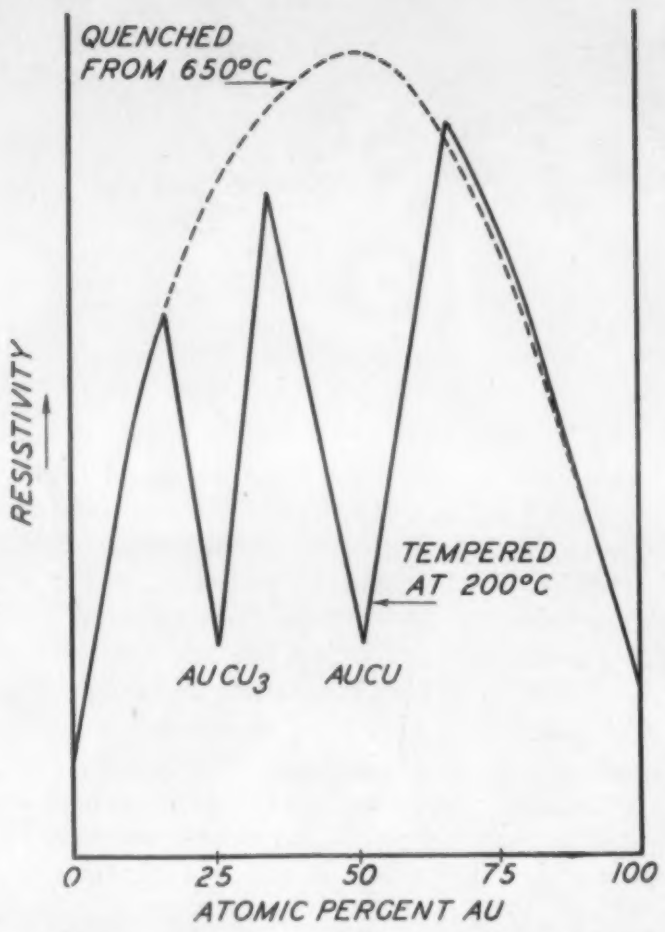


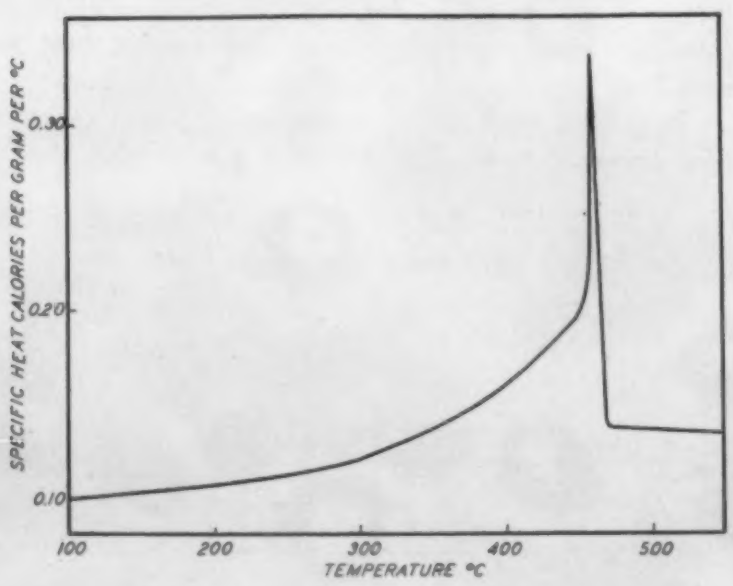
Fig. 6. Electrical resistance of Au-Cu alloys, disordered (quenched) and ordered (tempered). (Johansson and Linde).

data is illustrated by studies on β-β' brass,[22, 23, 24] particularly Sykes' recent curve of specific heat under equilibrium conditions reproduced in Fig. 7.

The dilatometer has been used frequently to reveal transformations of this type.[25, 26, 27] They can also in some cases be detected metallographically, as for example in AuCu,[27, 28, 29, 30] which shows a needle-like structure somewhat resembling martensite or Widmanstätten structures. This "recrystallizes" into a normal polyhedral structure upon annealing. In other cases, for instance Fe_3Al, there is said to be no metallographic evidence of transformation.[31, 32] Other properties are also affected in a less direct way: Magnetic properties,[24, 33, 34, 35] hardness, [28, 30, 36, 37] elastic constants.[36, 37, 38, 39, 40]

The degree of lattice deformation—for example, the amount of tetragonality in AuCu as expressed by the

Fig. 7. Specific heat of β brass. (Sykes).



axial ratio, c/a, of the lattice—is considered by some[2, 7, 8, 10, 41, 42, 43, 44, 45] to be coincident with ordering and to be a direct index of the degree of order. There has not been a uniformity of opinion on this point, however, for earlier investigators considered that the processes of lattice deformation and of segregation to ordered atomic positions are separate and independent mechanisms operating at different rates.[17, 46, 47, 48] It seems more reasonable to believe that tetragonality results directly from ordering, and that the difference in rates is apparent, arising from the lack of coherent ordering throughout the crystal, rather than real.

The Theory of Superlattices

Theoretical treatments of the phenomenon have been given by Borelius,[44] Borelius, Johansson and Linde,[49] Gorsky,[29] Dehlinger,[54] and Dehlinger and Graf,[46] chiefly on the basis of formal thermodynamic relations. It was considered anew by Bragg and Williams,[6, 19] Williams,[21] Bethe,[20] and Peierls[55] who as a group started with simple assumptions about atomic forces and calculated quantitative results that compared very favorably with experiment. This second series of papers is probably of more interest to the readers of this journal and will be discussed in greater detail in this report.

In an alloy of A and B atoms the energy of the crystals will be a minimum when order is complete and will be increased an amount V if a pair of atoms is interchanged so that an A atom takes a place that should be occupied by a B atom, and a B atom moves to a position that should be occupied by an A atom. In other words, V is the net amount of work required to effect this interchange. Under thermal agitation an equilibrium will be reached where the ratio of the number of atoms in their right positions to the number in wrong positions is equal to the Boltzmann factor $e^{-V/kT}$, where k is Boltzman's constant and T is the absolute temperature.

If V were a constant, independent of the degree of order in the alloy, there would be a gradual increase in disorder with rising temperature following an exponential curve that is frequently encountered in thermodynamics. This cannot be the case, however, for decrease in order must decrease the forces that tend to maintain order. The distinction between right and wrong positions for an atom, in fact, vanishes when disorder is complete and V then drops to zero. It is this dependence of V on order that is responsible for order decreasing at an accelerating rate as the temperature is raised, and that accounts for a critical temperature analogous to the Curie temperature where a magnetic material loses its ferromagnetism.

To make a theoretical calculation of the degree of order in equilibrium at each temperature, it is therefore necessary to assume a particular relation between V and the degree of order. For simplicity Bragg and Williams[6] assumed that V is proportional to the degree of order S (or $V = V_0S$), where S is defined as the fraction of the atoms that are in their right positions minus the fraction that are in wrong positions. This definition of S requires a knowledge of which positions in the crystal are right and which are wrong and applies to an organized order extending over long distances in the crystal; it is a "long distance" order.

An alternative conception of order has been worked out by Bethe,[20] Williams,[21] and Peierls,[55] and has also been

discussed by Hume-Rothery,[41] and concerns only atoms that are nearest neighbors. The order of neighbors, σ, or "local order" is defined by them as the probability of finding an unlike atom beside a given atom minus the probability of finding a like atom there. The equilibrium state at each temperature has been calculated using this definition and assuming that only the nearest neighbors of an atom interact with each other.

The statistical calculations show that even if interaction is limited to nearest neighbors, there will nevertheless be built up a coherent "long distance" order below a critical temperature; above this temperature there will be small ordered nuclei constantly forming and dissolving much as in a liquid.

The theoretical curve of Bragg and Williams for long distance order is shown in Fig. 8 for the case of equal numbers of ordered and disordered positions, as in AuCu, CuZn, and Fe_3Al. (The curve calculated by Bethe for long distance order is very similar but somewhat steeper just below the critical temperature T_c.) The critical temperature T_c is proportional to V_o and is given approximately by the relation $T_c = V_o/4k$ where k is Boltzmann's constant.

Starting with a superlattice in equilibrium at a low temperature, let us consider the amount of heat that will be required to raise the temperature successive intervals. At first the heat input will go entirely to increase the thermal motion of the atoms, and the specific heat of the alloy will be normal. As the temperature increases, however, an increasing amount of work will be required to move atoms from right to wrong places, and this will appear as an abnormal specific heat, which climbs to a maximum just below the critical temperature where the changes in order are most rapid. Above the critical temperature the specific heat would return again to normal were it not for the small residual nuclei of "local order" which persist for some distance beyond. As the experimental curve in Fig. 7 shows, the theory compares favorably with experiment.

Disorder makes a large contribution to the electrical resistance, superimposed upon the resistance due to thermal vibrations. Bragg and Williams' calculated curve of resistivity vs. temperature for AuCu in equilibrium is reproduced in Fig. 9 and compared with measured values obtained during a slow rate of cooling.[25] The experimental curve deviates from the theoretical because of the increasing sluggishness of diffusion at the lower temperatures, the alloy finally "freezing" into a state of partial order when atomic interchange becomes negligible.

The theoretical curve of order for $AuCu_3$ differs somewhat from the AuCu curve of Fig. 8 in that at the critical temperature there is a discontinuous jump from disorder to partial order, S jumping to about 0.4. As a result of this, there is an evolution of latent heat at this point (which is in accord with Sykes' thermal data)[24] and an abrupt increase in resistance. The actual resistance curve for the equilibrium condition in $AuCu_3$ shows this effect quite clearly,[16] as will be seen from Fig. 10. It is more or less obscured in ordinary heating and cooling experiments by various complexities: Order is not coherent throughout the whole of the individual grains,[16] diffusion is sluggish, particularly at the critical temperature,[6] and whenever the transition is from a cubic to a tetragonal lattice one might expect internal stresses to arise as the regions of local order grow into contact with each other.

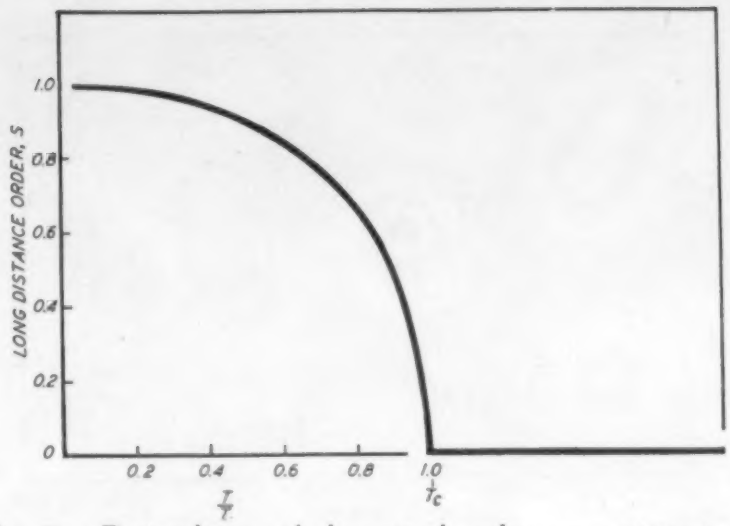
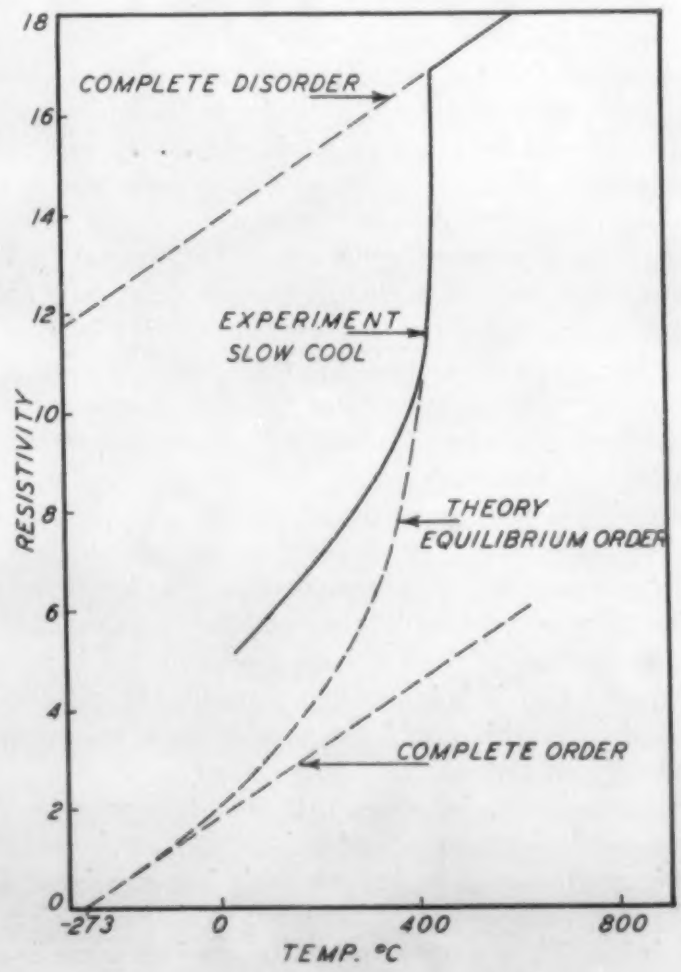


Fig. 8. Dependence of degree of order on temperature. (Bragg and Williams theory for long distance order).

Similarity Between Superlattices and Other Phenomena

Superlattices have a close parallel to ferromagnetism. The Bragg and Williams treatment of long distance order S is analogous to Weiss's theory of ferromagnetism, S corresponding to the magnetization and V to the difference in potential energy for the parallel and anti-parallel electron spins, while the treatment based on local order, σ, parallels the modern theory of ferromagnetism, with interaction assumed only between neighboring electron spins (except that quantum mechanics are not involved in calculations of order as they are in magnetism).[56, 57, 58] Another closely analogous case is the vibration and rotation of molecules in crystals such as the ammonium halides where there is a critical temperature above which all the ammonium radicals rotate, and below which the rotation is gradually replaced

Fig. 9. Electrical resistance of AuCu during slow cooling. (Kurnakow and Ageew data, Bragg and Williams theory).



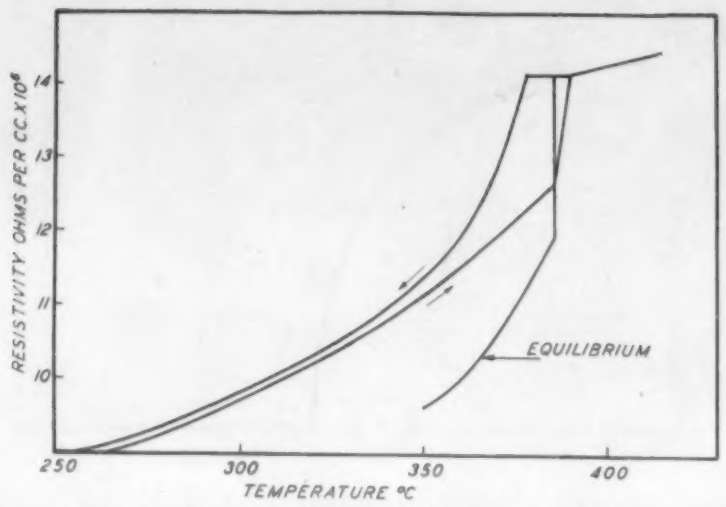


Fig. 10. Electrical resistance of $AuCu_3$ during cooling and subsequent heating at 30°C. per hour and at equilibrium. (Sykes and Evans).

by oscillation. Fowler has discussed the theory of these transitions.[59] In all these analogous phenomena there is a critical temperature which is properly called a Curie temperature, resulting from an ordering force that decreases with order.

The Rate of Approach to Equilibrium

Bragg and Williams have made some interesting calculations of the rate at which an alloy will approach its equilibrium degree of order at any temperature. They assumed that the rate of approach is directly proportional to the discrepancy between the actual and the equilibrium order. The constant of proportionality was taken as $1/\tau$, where τ is the "time of relaxation" of the alloy, the time required for the departure from equilibrium to be reduced to $1/e$ or 0.368 of its initial amount. A reasonable expression for τ is then $\tau = Ae^{W/kT}$, where A is roughly of the order of 10^{-12}, and W is the "activation energy" that a pair of neighboring dissimilar atoms must have in order to surmount their potential barrier and exchange positions.

This expression for the relaxation time permits an estimate of the range of states that can be produced in an alloy by different heat treatments. Rapid quenching will retain a degree of order characteristic of a high temperature, and annealing for several days will produce a degree of order characteristic of a lower temperature, but the calculations indicate that these two temperatures will differ only about 30 per cent (on the absolute temperature scale) because of the rapid change of τ with T. Bragg and Williams estimate from resistance curves that for $AuCu_3$, τ is one second at about 550 deg. C. which is above the transition temperature and accounts for the fact that complete disorder can be maintained by quenching. Prolonged annealing, on the other hand, would be expected to produce degrees of order corresponding to a temperature not much below 270 deg. C. where the equilibrium order S is approximately 0.75. In the case of Cu-Zn the rate of diffusion is so fast (τ so small) that it is impossible to retain the disordered structure by quenching, and the alloy at room temperature is always highly ordered.

It appears likely, however, that this treatment of the problem overlooks some complications that are important. There is much reason to believe (this has also been discussed under "Methods of Investigation") that as an alloy is cooled below T_c, a number of nuclei start to grow independently of each other and with a non-coherent relation to each other. Their growth must continue until they touch, and then they must coalesce until the whole of a grain—or the whole of some natural subdivision of a grain—contains a coherent array with no out-of-phase regions remaining unabsorbed. Recent experiments of Sykes and Evans[16] suggest that the rate of ordering within each nucleus may be as much as a thousand times faster than the rate of growth and coalescence of the nuclei. Once the coalescence has been completed, however, subsequent alterations in order seem to be at the rapid rate characteristic of a nucleus, indicating that such alterations do not produce any new anti-phase nuclei. It will be seen that the mechanism of onset of order is in many respects similar to the familiar one of recrystallization and coalescence in deformed grains, although the rates are different, and are affected differently by plastic deformation.

Phase Changes

The interaction between atoms may be so strong (V so great) as to make the virtual value of the critical temperature, T_c, lie above the melting point. Such is the case in those phases which show a superlattice structure at all temperatures in the solid state. Cu_3Sb seems to be an example with Fe_3Al structure, and AuZn is another with the CsCl structure.[60] The alloys with these characteristics more closely resemble true chemical compounds.

It will be seen that the whole range of intermetallic structures can be considered from this point of view. When atomic interactions are strong they may retain order, like a compound does, up to a temperature at which another phase has a lower free energy and begins to form; in the case of AgZn, for example, the new phase is another solid phase of different crystal structure, while in the case of AuZn the new phase is the liquid phase. With less intense ordering forces between the atoms the ordered arrangement may decrease gradually to a low value or to zero at the critical temperature. If V is very small—and this must be the case at low concentrations in terminal solid solutions, since any ordered array would put the stranger atoms far apart on the lattice—the critical temperature will be below room temperature, or at any rate so low that the atoms will not diffuse appreciably into their ordered positions.

The behavior of an alloy will thus be largely governed by two constants, the interaction energy, V_o, which is the net amount of work necessary to switch a pair of atoms into disordered positions in the fully ordered alloy, and the activation energy, W, that the atoms must acquire in order to make the exchange. Approximate values[6] for these in AuCu, expressed in electron volts, are $V_o = 0.3$, $W = 1.85$. The value W may also be converted to calories Q, ($Q = 23{,}054\ W$) and will then be seen to be of the same order as the heats of activation for diffusion in solid solution, recently summarized by Mehl.[61] It is also of the same order of magnitude as the heats of activation for recovery from cold work; for example in recent experiments at the Bell Laboratories[62] on permalloy the rate of sharpening of broadened X-ray diffraction lines has given the value $W = 1.7$ electron volts. But in making such comparisons of W it should be remembered that small differences in W correspond to large differences in rates, since W is related exponentially to the rates.

(Concluded on page 260)

COPPER-LEAD

Bearings from Metal Powder

—A NEW ART

by Erich Fetz

Formerly Research Metallurgist
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Now Research Metallurgist
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THE INCREASINGLY SEVERE SERVICE conditions encountered by bearings in modern internal combustion engines demand the development of new anti-friction alloys.[1] Leaded bronzes, cadmium-silver and, more recently, straight copper-lead alloys are replacing babbitts in many applications, and therefore, assume considerable metallurgical importance. The superiority of copper-lead over tin-base alloys in regard to tensile and compressive strengths is the more pronounced the higher the operating temperature. Even at temperatures at which the white bearing metals are molten, copper-lead bearings may be successfully applied, under emergency conditions. Their thermal conductivity[2] is several times that of babbitts and the frictional coefficient[3] is much lower. The anti-friction qualities of lead are well illustrated by its use as a 'lubricant" in wire drawing. Unlike the leaded bronzes, straight copper-lead linings require no hardened shafts. The resistance to pounding, which naturally decreases with increasing lead contents, is not a factor within the present commercial lead range. Superior fatigue strength at low and at elevated temperatures is also claimed to be an important factor in the replacement of babbitts by copper-lead.[4]

Current Objections to Copper-Lead Bearings

Despite the unquestionable superiority of copper-lead alloys in heavy duty service, their more general adoption is greatly hampered at present by manufacturing difficulties.[5] The lack of mutual solubility of copper and lead in the solid state represents the principal source of this trouble[6] aggravated by the widely separated specific gravities of both metals. And even though liquid mixtures with less than 38 per cent are completely miscible, nearly pure copper crystals separate from a liquid copper-lead melt on passing through the temperature range bounded by 1083 deg. C. (melting point of copper) and 954 deg. C. (monotectic temperature), while the remaining lead solidifies at 327 deg. C. The liquid phase of nearly pure lead tends to coalesce into relatively large masses during solidification and the aggregate shows marked segregation of lead at room temperature; this tendency towards lead segregation is more pronounced the higher the lead content. The temperature relationship of the specific volumes shows that copper has a larger volume shrinkage than lead; the latter is drawn in between the copper dendrites by a capillary effect (phenomenon of inverse ingot segregation). The resulting unsoundness explains why the theoretical densities of copper-lead mixtures are often not in agreement with those measured. Lead segregation may be reduced, or prevented entirely, by rapid cooling through the freezing range, and the cooling rate becomes more important as the lead content is increased. Above 38 per cent lead, copper and lead are immiscible even in the liquid state and form 2 separated liquid phases before any restraining network of a solid phase can form.

The main object in the manufacture of copper-lead bearings has thus been to prevent, by means of rapid cooling, pronounced separation of both constituents. A great number of patents have been granted to inventors aiming at drastic chilling of molten copper-lead and at good adhesion between shell and bearing.[7] Because the presence of impurities tends to check the pronounced lead segregation[8] in alloys with more than 25 per cent Pb, some improvement has been attempted by additions of sulphur, zirconium[9], tellurium and selenium[10]; additions of nickel are also employed. According to the copper-nickel-lead diagram[11], the addition of 3-5 per cent nickel closes the miscibility gap of the binary copper-lead system resulting in uniform solidification and regular distribution of lead in copper. Sulphur has a similar effect, additions of 0.67-1.60 per cent being sufficient. It has also been claimed that the use of fluxes suppresses the lead segregation to a notable extent[12].

One job where no apparent difficulties are encountered is that at the Ford Rouge plant in which a low carbon, cold-rolled strip steel, 0.068 in. thick, is coated continuously by passing it through a copper-lead bath at 1150 deg. C.[13] However, the copper-lead mixture contains only 30-35 per cent lead (63-68 per cent copper, 0.5 per cent iron, 1-1.5 per cent nickel), a relatively low value when we consider that the atomic weight of lead is 3¼ times that of copper. Serious difficulties in the production of copper-lead bearings begin at about 35 per cent lead.

The production of satisfactory joints is also a problem with the lead-rich alloys, because of their larger thermal expansion, higher solidification temperature and more rapid oxidation as compared to ordinary babbitts. In order to obtain a good bond with a steel backing, it is necessary to have more than the average percentage of copper at the backing/bearing interface; on the other hand, a higher lead

content at the bearing surface greatly improves the bearing properties. The copper crystals should grow dendritically on and vertically to the bearing shell and should extend from the surface to the backing to induce greater strength. However, a 'streaky" or columnar structure of lead equal in length to the entire bearing thickness has been definitely established as a cause of failure. The 70/30 copper-lead alloy is frequently claimed to be "too hard," with consequent excessive wear of the shaft. Microscopic examination, however, will frequently disclose an undesirable micro-structure as the immediate seat of trouble.

The natural tendency to apply the prior art to new developments has led to many disappointments in the application of copper-lead anti-friction alloys. Thus, many lubricants that had given excellent service with babbitts proved to be entirely unsuitable for copper-lead bearings. Oils best suited to babbitt lubrication were of the fatty type, whereas such 'oils when used with copper-lead introduce serious corrosion and erosion problems, chiefly the "washing" away of lead. These early difficulties in the lubrication of Cu-Pb bearings have largely been solved by the use of special compounded and mineral oils.[14, 15]

Attention to mechanical features, such as design and operating practice, also has provided improvement in the life of Cu-Pb bearings. Most important have been better lubrication, and more accurate fitting of the bushing in comparison with ordinary babbitts. Shortening of the length of the rubbing surface together with the use of larger diameters have also been steps in the right direction. Ability to carry shock loads, reduction of bending stresses, better heat dissipation and greater resistance to flow are observed with reduction of thickness of lining backed by a strong shell.

Powder Metallurgy Attacks the Copper-Lead Problem

Inasmuch as many of the objections to copper-lead had arisen from difficulties associated directly with pouring and solidifying this type of bearing, preparation of copper-lead bearings from metal powders appeared to be very attractive, as this branch of metallurgical science (1) circumvents melting and casting altogether, (2) provides more easily the most advantageous distribution of lead and copper and guarantees the continuity of the copper matrix, and (3) permits the production of bearings with lead contents higher than can possibly be obtained with conventional melting and casting methods. In addition, only a small amount of lining metal is required for a vitally important engine member, so that the additional production costs of powder metallurgy become of secondary importance. Finally a successful precedent exists in the "synthetic" production of self-lubricating bearings which either contain graphite in uniform distribution or are so porous as to absorb a large volume of oil.

Experiments with Metal Powders

The following is a brief account of the author's experiments to produce copper-lead bearing alloys by utilizing metal powders. At first intimate mixtures of lead and copper powder were hydraulically compressed at 5 to 50 tons per sq. in. and then annealed in hydrogen at rising temperatures. Below the melting point of lead, no sintering of the copper particles occurred even after prolonged heating, and the samples could easily be scratched with the finger nail. Above 327 deg. C., lead segregated out even with the mixture comparatively low in lead. All attempts, therefore, based on the use of mechanical mixtures of lead and copper powder resulted in complete failure. It was evident that temperatures *materially higher* than 327 deg. C. are essential for attaining a true metallic bond between adjacent copper particles.

This prerequisite was fulfilled by employing copper-coated lead powder prepared in the following manner[16]: 250 g. of 100 mesh lead powder is added to a solution containing 1000 cc. water, 10 cc. acetic acid and 200 g. copper acetate, at 85 deg. C. The lead should be added as a suspension in water. Stirring is continued until all the copper has come out of solution. The solution is decanted off and the coated powder is thoroughly washed with water and anhydrous ethyl alcohol, followed by drying (which may be aided by ether) and screening. The thickness of the copper coating can be varied by increasing the ratio of the copper content of the solution to the amount of lead employed. Recently copper plating by electrolysis has come into the foreground.

Because they tended to reoxidize, the copper-coated lead powders were first annealed in hydrogen at temperatures approaching the melting point of lead. The weight losses varied between 3.5-6.5 per cent, and the powders assumed a rosy-red, lustrous appearance.

In view of the efficiency and economy of the spraying process, this production method was investigated in a great number of experiments, using a solution of 6.5 g. vinylite in 1000 cc. acetone as the suspension medium. Preliminary tests made with various concentrations and at different air pressures indicated these proportions to be most suitable.

The sprayed layers often exhibited noticeable cracks after drying and tended to flake off at room temperature before thermal treatment. A sufficiently firm bond, resistant to bending, could not be obtained even by hydrogen annealing at temperatures exceeding the melting point of lead by several hundred degrees. It appeared that the difference in thermal expansion coefficients between the steel carrier and sprayed copper-lead mixture caused the latter to tear loose at an early stage. Spraying onto roughened copper and bronze carriers was of no avail either. Also, the suspension medium seemed to leave, after evaporation, an insulating film on the sprayed powder particles, thus impairing the intimacy of contact at the interface between the two diffusing bodies. Some of the sprayed coatings appeared to be quite porous. Although rolling after annealing completely eliminated this deficiency, the lack of adhesion was not overcome, long-time annealings being ruled out as uneconomical. Furthermore lead sweat was noticed on some samples at much lower temperatures than with pressed copper-coated lead powders.

German research[17] on the interdiffusion between sprayed coatings and mild steel carriers yielded poor bonds owing to the obstruction offered by oxide films at interfaces and the slow atomic diffusion rates, although much longer annealing times and considerably higher temperatures were applied than in the present experiments.

Strips from Copper-Coated Lead Powder

Further spraying tests were abandoned since another way led directly to the solution of the problem, namely, pressing

of copper-coated lead powder into strips, sintering in a hydrogen or neutral atmosphere and bonding onto a metallic carrier. Copper-lead bearings so prepared, and containing 20-35 per cent lead, can be heated to 900 deg. C. without lead sweat; a mixture containing 45-55 per cent lead can be heated to 750 deg. C. At these elevated temperatures, adhesion forces come into play, and interaction by diffusion of atoms readily takes place. Thus a well-sintered metallic body, quite susceptible to bending and cold rolling, is secured. It was found, for example, that reductions of 50 per cent in thickness were possible with an alloy containing 43 per cent lead. A systematic variation of strength and flexibility over a wide range could be produced by varying the copper content and also the amount of strain hardening in rolling. Reannealing of cold-rolled copper-lead strip in hydrogen at temperatures 100-150 deg. C. below the initial sintering temperature did not cause lead segregation. Thus a method for the preparation of workable copper-lead strip that could be annealed without damage had been found.

The second major problem was to bond these copper-lead strips to a backing sheet. As was the case with sprayed coatings, no firm bond could be obtained by combining the two operations, sintering and bonding. Even when the powder was pressed into ragged backing sheets of comparatively low melting point, and both bodies were pressed firmly together, the degree of penetration after several hours at 700-800 deg. C. was not sufficient to prevent parting on bending. This difficulty can, of course, be circumvented by pressing the powder into carefully prepared backs possessing the final shape of the half-shell bearing. In this manner sintering and bonding may be carried out simultaneously in hydrogen at temperatures higher than 700 deg. C.

One successful method of bonding the sintered copper-lead strip onto copper or bronze backing sheets is by diffusion annealing at the highest possible temperatures. The copper-lead strip is rolled under slight pressure on carefully cleaned copper or bronze sheet roughened by sand-blasting, electrodeposition or by fusing on of coarse copper powder. However, the applicability of this method is limited, for, on prolonged heating, the samples with higher lead content exhibited lead sweat.

An intermediate layer of tin was necessary to bond the sintered bearing onto the steel sheet. This was done by dipping the latter into liquid tin using as flux a zinc-ammonia solution and then pressing the copper-lead strip onto the backing. The strength of the finished bearing can be further improved by heat treatment.

Copper-Lead Composite Bearings

It has been observed that a preponderance of copper at the bearing shell/lining interface results in a better bond.[5] In binary systems the diffusion coefficients in either terminal solid solution are greater in the solid solution with the lower melting point; thus the diffusion of gold in lead is 26,000 times that of lead in gold,[18] while the self-diffusion of lead is about twice as great as that of gold into lead.[19] Analogous conclusions should hold for copper-lead and for the self-diffusion of copper, in view of practical experience calling for an excess of copper at the backing interface irrespective of whether a steel, copper or bronze shell is employed.

Composite bearings were made consisting of a pure copper powder bottom and a copper-coated lead powder surface. Both powders were pressed simultaneously in the hydraulic press, sintered at temperatures higher than 700 deg. C. and slightly cold-rolled to eliminate warping and shrinkage effects. The following advantages are possessed by these duplex bearings:

(1) The production costs of the powder bearing are much reduced, as only the bearing surface consists of the most expensive part, the copper-coated lead powder.
(2) The heat dissipation is improved by using a solid copper bottom layer.
(3) The strength of the bearing is greatly increased.
(4) The wettability of the copper bottom with respect to tin is superior to a sintered copper-lead strip, mechanically cleaned before bonding.
(5) The lead concentration at the bearing surface can be easily adjusted to any specific use. It can be made sufficiently high to allow for the so-called "whipping action" without sacrificing the necessary strength, toughness and wear resistance in the rest of the bearing.

The possibilities inherent in these duplex bearings have not yet been fully utilized.The use of a solid solution type alloy like copper-nickel for this intermediate layer provides a stronger bond because of the alloying action of mutual diffusion and the absence of inter-metallic compounds.

Babbitts may vary in service performance, depending on the size and distribution of the hard SnSb (Cu_3Sb, Cu_3Sn) crystal constituent embedded in the soft matrix. If the structure is too fine, the babbitt may be brittle[20]. Based on this observation, serious objections have been raised as to the suitability of copper-lead powder bearing alloys "due to the extremely fine dispersion of the soft lead powder particles and their enclosure in the copper shell."

Lead-Soaked Copper Sponge

The maximum lead particle size applicable for copper-coating and for the manufacture of synthetic copper-lead bearings (and therefore, the potential importance of the foregoing objection) has not yet been established. Whatever the outcome, powder metallurgy is already approaching the copper-lead bearing problem from a new angle, which may be sketched briefly. A coarse-grain copper powder is mixed with a volatile non-metallic matter, hydraulically compressed and heated in hydrogen to about 900-1000 deg. C. The copper particles sinter to a sponge-like body, the porosity of which is mainly regulated by the grain size of the copper particles and the amount of volatile matter. The latter emerging from the copper cake opens up small channels throughout the whole mass. The copper sponge so produced is then "soaked" in liquid lead in a vacuum. No air trapping and a very advantageous distribution of soft lead globules in a solid copper skeleton result. In addition, no difficulties exist in providing for a larger amount of lead at the bearing surface and a preponderance of copper at the shell bearing interface. The "sponge" principle itself is not new; the soaking of porous, synthetic bearings with oil in a vacuum has been successfully applied to the so-called "oil-less bearings," while copper is sucked by capillarity action into the voids of a tungsten briquette in the production of "Elkonite".[21]

Conclusion

The difficulties involved in the casting of straight copper-lead bearing alloys with more than 30 per cent Pb are considerable. Powder metallurgy avoids lead segregation altogether, permits great latitude in the relative distribution of lead throughout the bearing and provides a more suitable bonding interface for the backing sheet. The most favorable results obtained so far were by sintering in hydrogen at 700-800 deg. C., a pressed strip consisting of a copper powder layer at the bottom and a copper-coated lead powder, containing 40-55 per cent Pb, at the top.

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Superlattices

(Concluded from page 256)

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Diffusion in Solid Metals—III

ADDENDUM TO A CORRELATED ABSTRACT

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(Publication Approved by the Directors)

In the May and June issues of METALS AND ALLOYS *there was published a correlated abstract on this subject by Mr. Krynitsky.*

The author regrets that the paper by Dr. Van Liempt was not included in the original abstract and therefore offers this addendum to this original because he feels it warrants this attention—Editor.

IT HAS BEEN POINTED OUT that the relation

(I) $D = \frac{Q}{Nh} a^2 e^{-Q/RT}$ proposed by Dushman and Langmuir[1] as a universal equation for adsorption in crystalline solids, is probably a more nearly correct interpretation of the diffusion phenomena. In this connection it would probably be of interest to note that in one of his papers, not mentioned in my abstract, Van Liempt presents a very interesting discussion[2] of his formula[3] versus Dushman-Langmuir equation.

In formula (I) N and h are respectively the Avogadro's number and the Plank constant and a is the spacing between atoms in the crystal. Inserting numerical values $\left(\frac{1}{Nh} = 1.05.10^{10} \right)$ this becomes[4]

(II) $D(cm^2/sec) = 1.05 \times 10^{10} \cdot Q\, a^2 e^{-Q/RT}$

where Q is expressed in gram-calories per gram atom, a in cm, R-gas constant and T absolute temperature. Van Liempt compares equation (II) with his formula (III).

(III) $D\ (cm^2/sec) = \frac{8}{3\pi} p^2 \nu e^{-Q/RT}$

where ν is the characteristic monochromatic atom frequency of metals in second and $p = a =$ minimum spacing between atoms in the crystal. Taking values of

$p^2 = a^2$ of order $7\ 10^{-16}$
$\nu =$ " " $5\ 10^{12}$
$Q =$ " " 20000 to 100000 cal.

Van Liempt finds that multiplication factor in formula (II) is 15.10^{-2} (cm^2/sec) to 70.10^{-2} (cm^2/sec) or 13000 60000 (cm^2/day) whereas, according to his formula (formula III) this factor is $3.5.10^{-3}$ (cm^2/sec) or 302 (cm^2/day). Considering some data presented by different authors and given in the table below, Van Liempt states that this factor is 50 to 200:

Au in Ag	$D(cm^2/day)$	$46\ e^{\frac{-29800}{RT}}$
Cu in Au	$D(cm^2/day)$	$91\ e^{\frac{-27400}{RT}}$
Cu in Ni	$D(cm^2/day)$	$90\ e^{\frac{-35500}{RT}}$
Mo in W	$D(cm^2/day)$	$52\ e^{\frac{-80600}{T}}$
Cd in Pb	$D(cm^2/day)$	$182\ e^{\frac{-15522}{RT}}$

Therefore he concludes that the practical factor is from 1/2 to 1/6 of his factor and from 1/100 to 1/1000 of the factor of formula (II). On the other hand, Van Liempt states, it was found by v. Hevesy in his experiments on self diffusion of lead that

(IV) $D(cm^2/day) = 576000\ e^{\frac{-28050}{RT}}$

Basing on this equation one may note that Van Liempt's factor is around 1/1000 and Dushman-Langmuir's factor is about 1/20 of the practical factor.

v.Hevesy who recognized this discrepancy explained that high velocity of self-diffusion was due to a certain chain-mechanism. Inasmuch as this problem is not solved as yet, Van Liempt believes that no data obtained from the experiments on self-diffusion should be used in calculations.

With reference to the merit of Dushman-Langmuir formula it would seem appropriate to mention that, as it has been recently shown[5], calculation of Q from one value of D in numerous systems indicates that in every case the best diffusion data are in accord with that formula.

It is evident that a great deal more work must be done before this problem will be clarified.

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A LETTER TO THE EDITOR

S. A. E. Steel Specifications

To the Editor: The pithy and pertinent editorials in METALS AND ALLOYS are always a matter of intense interest to the writer, and seldom have they failed to hit the bulls-eye. It is therefore with a great deal of regret that I have to utter a strong proest concerning what I deem to be a serious misconception of the organization and purpose of the S.A.E. Iron and Steel Division.

Toward the conclusion of your editorial entitled "Let's Split Some Hairs" in the June issue of METALS AND ALLOYS you state:

> Of course, the S.A.E. could finish what it started, but since it is more of a steel user than a steel producer organization, some society representing both groups might distribute the burden more equitably.

As a matter of fact, the steel producer representatives form the largest single unit of the many interests represented on the S.A.E. Iron and Steel Division, as will be seen from the following tabulation:

13	members	represent	steel producers.
3	"	"	alloy.
7	"	"	auto and tractor producers.
3	"	"	aircraft producers.
4	"	"	accessory & machine tool builders.
1	independent—chairman.		
31	total membership.		

The purpose that actuates the S.A.E. Iron and Steel Division was set forth briefly in the introduction to the last revision of these specifications—S.A.E. *Journal,* April, 1935, page 15, from which a few pertinent paragraphs are quoted:

> One frequently hears the criticism—"There are too many steels included in the S.A.E. specifications." Looking at the matter from the standpoint of the ultimate consumer that statement may be true. The Iron and Steel Division is not oblivious to the fact that an automobile, a farm tractor, a Diesel engine, a printing press or even the latest model of streamlined locomotive and train can be built with but a small fraction of the number of steels covered by these specifications.
>
> The S.A.E. Iron and Steel Division, however, has no mandate to dictate to the steel user just what steel he shall use for his particular application, nor has it any mandate to limit the steel maker as to the compositions he shall make. Its job is to bring the various users and makers of each type or grade to an agreement upon a common chemical specification for that steel. It does require that a steel shall have attained a significant volume of production or be generally recognized as necessary before it is established as an S.A.E. steel. Thus, while these specifications provide 109 steels and alloys, the various compositions for a single steel have been reduced from as many as nine to one.
>
> Each user has his preferred steel compositions and each steel company has its particular group of steels upon which it specializes and endeavors to develop continually in the direction of improved quality. To attempt at this time to reduce substantially the varieties of steels in these specifications would not be desirable standardization. Its effect would be to stifle progress.

I know you have no desire to deprecate the work of the S.A.E. Iron and Steel Division, but our members do wish to have their representative type of organization recognized. The work that was published in the form of probability curves by Janitzsky was sponsored and directed by the Division and participated in by both the laboratories of steel makers and steel users. However, do not overlook the fact that shortly after that work was done, all industry entered an era that made it difficult to sell any boss, steelmaker, auto maker, or any other maker, the idea of embarking upon the stupendous program required to develop reliable test data for even the more common S.A.E. alloy steels. It is possible that Washington may attempt to tell us what steels we shall use in the near future but, passing that catastrophe, the S.A.E. Iron and Steel Division is ready to shoulder what it considers its responsibility at any time the conditions are propitious for such a labor.

With sincere regards, I remain,

F. P. GILLIGAN.

Chairman,
S.A.E., Iron and Steel Div.

Editor's Note: We were of course aware that the Iron and Steel Division of the S.A.E. has well-balanced producer and consumer representation. The membership of the society as a whole is, however, obviously so overwhelmingly made up of users who have so many interests which the society serves and so many problems on which the society tries to throw light, that to the S.A.E. as a whole, it would appear to us, the problem under discussion must be just another one of many equally pressing problems. The Iron and Steel Division, as Mr. Gilligan's letter shows, appreciates its opportunity and responsibility for the further clarification of the properties of steels. We wonder, though, if the S.A.E. as a whole appreciates the work of its Iron and Steel Division as much as the strictly metallurgical fraternity does.

It is encouraging to know that the program is only suspended and not abandoned. The reasons for the suspension, as given by Mr. Gilligan, were valid ones, but the problem has become more rather than less pressing during the hiatus, and it would appear that early resumption of the work could be economically justified. That is, with taxes as they are today, the net cost to the stockholders of doing the needed work would be less than it would have been under the conditions obtaining at the time of Janitsky's reports.

The center has the ball ready to snap after a long time out. We'd like to hear the referee blow the whistle to start play once more. The half who made the long run before, but was knocked out by the depression seems to be O.K. now and we'd like to see him take the ball again, with the other societies and groups active as interference, but if the S.A.E. ball-carrier shouldn't see open territory ahead, a lateral to some other runner might be good strategy. We're more interested in seeing the ball move forward than in who carries it.

Nobody will cheer Gilligan's committee more loudly than we when the goal line is passed. But there are still some 70 yards to go. Here's hoping that we get out of the huddle and get the ball into play quickly.—H. W. G.

The Hydride Process—I

by Peter P. Alexander

General Manager
Metal Hydrides, Inc., Clifton, Mass.

THE HYDRIDE PROCESS HAS FOR ITS OBJECT the production, on a commercial scale, of various hydrides and the utilization of their special properties in the production of pure metals, alloys and pure active hydrogen.

The hydrides, that is, the compounds of various elements with hydrogen, have been known to chemists for a long time but it is only recently that an intensive study of these interesting compounds has revealed the importance of this group from the standpoint of industrial application.

The elements Li, Na, K, Rb, Cs, Ca, Sr and Ba, enter into combination with hydrogen in only one proportion, forming only one definitely established hydride, such as LiH or CaH_2, for example. Other elements such as boron or silicon form with hydrogen a series of compounds. Therefore, the number of known hydrides is considerable.

How Hydrides Were Discovered

The story of the discovery of some hydrides is one of the typical adventures of research. The discovery of the boron hydrides is probably one of the best illustrations of the way in which a little change in experimental technic is sufficient to determine either complete failure or glowing success. The determined search for boron hydrides by such outstanding investigators as Wohler, Daville[1] and Moissan[2] completely failed to obtain boron hydride from aluminum boride and hydrochloric acid. Yet Stock and his collaborators[2, 3] by using only slightly different technique, revealed a completely new field and established the fact that boron forms a chain of compounds analogous to the hydrocarbons.

The number of hydrides prepared by different investigators is considerable, and the identity of the volatile hydrides, such as most of the hydrides of boron or silicon, is definitely established, since they can be isolated by fractional distillation. The identity of the hydrides of the elements of higher atomic weight cannot be established with equal certainty. The hydrides of Ca, Ba, Sr, Ti, Zr, Th, Cd and Ta are solids and usually decompose before reaching the melting point. Under varied conditions the amount of hydrogen present in the compound may vary and therefore the chemical formulas by which different investigators propose to represent them also vary.

However, as the knowledge of these compounds increases it becomes evident that the hydrides are not mere alloys or metals holding hydrogen in occluded state, but are true compounds possessing different physical and chemical properties than the elements from which they have been produced.

For instance, such good conductors of electricity as Li, Na, K and Ca, when allowed to absorb a sufficient amount of hydrogen, are converted into crystalline bodies which do not conduct electricity, and in fact may even be considered as insulators. The melting points, the sublimation points, as well as the chemical properties of the formed hydrides are very different from those of the metals from which they have been derived.

Properties of Calcium Hydride

One of the most interesting and best known hydrides is calcium hydride (CaH_2). If hydrogen is passed over calcium at a temperature of about 400 deg. C., the reaction between these two elements starts and proceeds with a large evolution of heat, until all the metallic characteristics of calcium disappear. The resulting compound is a dense, crystalline body which has a higher specific gravity than calcium, has a very much higher melting point, and can be easily pulverized into fine powder.

The most interesting properties of calcium hydride are its behavior towards water, oxygen and nitrogen. With water or even slight traces of water vapor, it reacts instantly even at room temperature. But in the absence of moisture it does not react with either oxygen or nitrogen, even at the temperature of dull red heat. As it was shown by H. Moissan[4], the discoverer of this hydride, it can be calcined in dry hydrogen at the temperature of red heat for several hours without any loss or gain in weight.

The heat of formation of calcium hydride as shown by A. Guntz and Basset[5], is 46,200 calories per mol. More recently C. B. Hurd and K. E. Walker[6] gave the heat of formation as 51,100 calories per mol.

Reduction of Refractory Oxides

The properties of calcium hydride have been utilized in the Hydride Process for the reduction of refractory oxides.[7]

Since calcium hydride can be easily pulverized in the jaw crusher, it is mixed in the usual tumbling barrel with a refractory oxide such as titanium oxide, and fed into a furnace heated to 900-1000 deg. C.

At a low temperature calcium hydride does not react with the oxide but above red heat it gradually dissociates into nascent hydrogen and nascent calcium with the result that the refractory oxide is completely reduced to metal.

Since the heat of different reactions taking place in the furnace almost balance one another, there is no great excess of heat evolved, and unlike the Thermit Process, the reaction proceeds gradually with the temperature seldom exceeding 1000 deg. C. The result of such a low temperature reduction is that the products of the reaction come, not in a fused mass, but as a fine powdered mixture of CaO and TiH_2 which can be degassed and gives pure metal containing only a small amount of hydrogen. The grain size of the produced metal is about 300 mesh.

The heat of formation of other hydrides, with one exception, is lower than that of calcium hydride, but in every case it is quite appreciable. This fact has been utilized in the Hydride Process for the better control of the reactions involved in the production of chemical compounds.

Calcium Hydride Directly from Lime

One of the interesting illustrations of such methods is the production of calcium hydride directly from lime.[8]

Calcium oxide under ordinary conditions is such a refractory oxide that it can not be reduced at 1000 deg. C. by any reagent. For example, if calcium oxide is heated with magnesium, the reaction shown below cannot take place since the heat of formation of calcium oxide is greater than that of magnesium oxide:

$$\underset{-151{,}710 \text{ cal.}}{CaO} + Mg = Ca + \underset{+\ 145{,}760 \text{ cal.}}{MgO}$$

However, if the calcium oxide is treated with magnesium in hydrogen, then the reaction does take place. Thus:

$$\underset{-151{,}710 \text{ cal.}}{CaO} + Mg + H_2 = \underset{+\ 46{,}200 \text{ cal.}}{CaH_2} + \underset{+\ 145{,}760 \text{ cal.}}{MgO}$$

The excess of heat of reaction, even if we accept the lowest given value for the heat of formation of calcium hydride, is 40,250 calories. Therefore, the reaction goes on to completion. Other reactions also take place in hydrogen much more readily if a corresponding hydride is being formed.

The calcium hydride obtained by this method is contaminated with traces of magnesium which alloys very readily with calcium, yet for many purposes such a product is entirely satisfactory.

Other Hydrides

The use of other hydrides such as zirconium hydride and titanium hydride gives equally interesting possibilities. In fact, the numerous hydrides, some of which are gases, others liquids, and still others stable solids, offer an almost unlimited choice, and practically any requirement can be met by the selection of a hydride with some particular physical and chemical properties.

(To be continued)

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A LETTER TO THE EDITOR

Hardness of Metals

To the Editor: In the book review section of the June issue of METALS AND ALLOYS, p. MA 385, there is a review of the book entitled "Hardness of Metals" by F. C. Lea. In this review it is stated: "For example, curves are given showing that with a worn Rockwell diamond cone, Rockwell C values some six points low were obtained over most of the range, as compared with readings with a new cone."

As manufacturers of the "Rockwell" tester we were vitally concerned with this reference in Professor Lea's text and we wrote Prof. Lea a rather lengthy criticism of the book and we are sending you herewith an extract from this letter which refers to his comments on a worn penetrator.

> "On page 52 you refer to results obtained with a "worn" and new diamond penetrator and show the values in Fig. 29 which average 5 to 8 points low with a 'worn' penetrator as against a new penetrator. We cannot understand this. We have never in our many years of experience with diamond penetrators and with the Rockwell tester run across such a condition. It is possible that a diamond might wear sufficiently to cause a somewhat lower reading but it would be a matter of tenths of a point and not several points. It would seem as if you must refer to a broken penetrator where you specify a 'worn' penetrator, or perhaps you were using a penetrator which had a poor shape from the beginning such as those plotted in Fig. 26. Poorly shaped diamonds would very easily give you readings as low as you report but a diamond ground to 120 deg. angle with a 0.2 mm. radius truly tangent would under no circumstances cause such readings according to our experience and our knowledge of the Rockwell tester and diamond cone penetrators, except due to chipping.
>
> "We have examined many cones which have made over 1,000,000 tests and they have not begun to show variation. We have here in our laboratory penetrators which we have used almost continuously since we first started in this work around 1922 and they are still reading, as closely as we can determine, the same as when we originally used them. We would appreciate seeing one of our penetrators in such worn condition that it would give such low readings Whether or not the penetrator which you refer to as being worn is really worn, or broken, or was badly shaped from the beginning, we do not know; but we do feel most strongly that it is wrong to use and publish tests made with an abnormal penetrator such as this one obviously is.
>
> "If, as is probable, your 'worn' penetrator was actually broken, which you could determine certainly under good magnification, then how could any corrective chart be established, for no two diamonds break similarly and even one diamond, once it had started to break could not be trusted at all.
>
> "You must keep in mind that breakage at the tip, while not greatly affecting hardness determined by dividing load by area, as employed in Brinell testing, will definitely affect the Rockwell as it is not a $\frac{\text{Load}}{\text{Area}}$ machine to the same extent. The zero setting for depth reading on the Rockwell is vital and yet would be grossly in error with a broken tip. This is due to the fact that Rockwell readings are based upon increment of depth with increment of load and not upon total depth due to only major load.
>
> "The life of a 'Brale' is limited and it must be replaced from time to time. This is due to breakage and not wear."

In fairness to the large number of Rockwell users who read METALS AND ALLOYS we feel it would be to their interest for you to call the above to their attention.

V. E. LYSAGHT.

Wilson Mechanical Instrument Co., Inc.,
New York City

Something was undoubtedly haywire with Lea's Rockwell. His conversion curves to Vickers and Shore are way out of line with all others.—H.W.G.

STEELS FOR Turbine Rotor Forgings AND THEIR HEAT TREATMENT

by N. L. Mochel

Metallurgical Engineer,
Westinghouse Electric & Mfg. Co., Philadelphia.

IN THE AUTHOR'S POSSESSION is a little engineering booklet dealing with steam turbines, printed in the year 1905, which has the following introductory statement: "The opening of the present century was marked by no more important event in the history of American industrial development than the general introduction of the steam turbine for power service."

Early History of Turbines

The reaction turbine principle had been demonstrated by Hero of Alexandria in 120 B.C., and the impulse turbine principle by Branca of Italy in 1629. Small turbines of the reaction type had been built by Avery in Syracuse in 1833 to 1836. Sir Charles Parsons had produced his first commercial turbine in 1884. It was not until the closing years of the nineteenth century that real development in this country was instituted.

In 1901, the largest steam turbine then in commercial use in the United States was installed at Hartford, Conn. This was of 2000 k.w. capacity, operating at 1200 r.p.m., with steam at 155 lbs. and total temperature slightly over 400 deg. F. By 1905, when the above quoted statement was made, turbines up to 10,000 k.w. capacity were possible, with pressures up to 175 lbs., and total temperatures not over 500 deg. F.

In the 30 odd years that have passed since that time, engineering history has recorded the rapid developments in capacity, in reliability and efficiency, and in wide-spread adoption of the steam turbine. Turbines up to 165,000 k.w. capacity on a single shaft have been built and are in successful operation, and units of even larger capacity have been built on two or more shafts. A number of turbines have recently been built and are building which take steam at 1200 lbs. and 950 deg. F. total temperature.

In the marine field, from the sensation caused at the

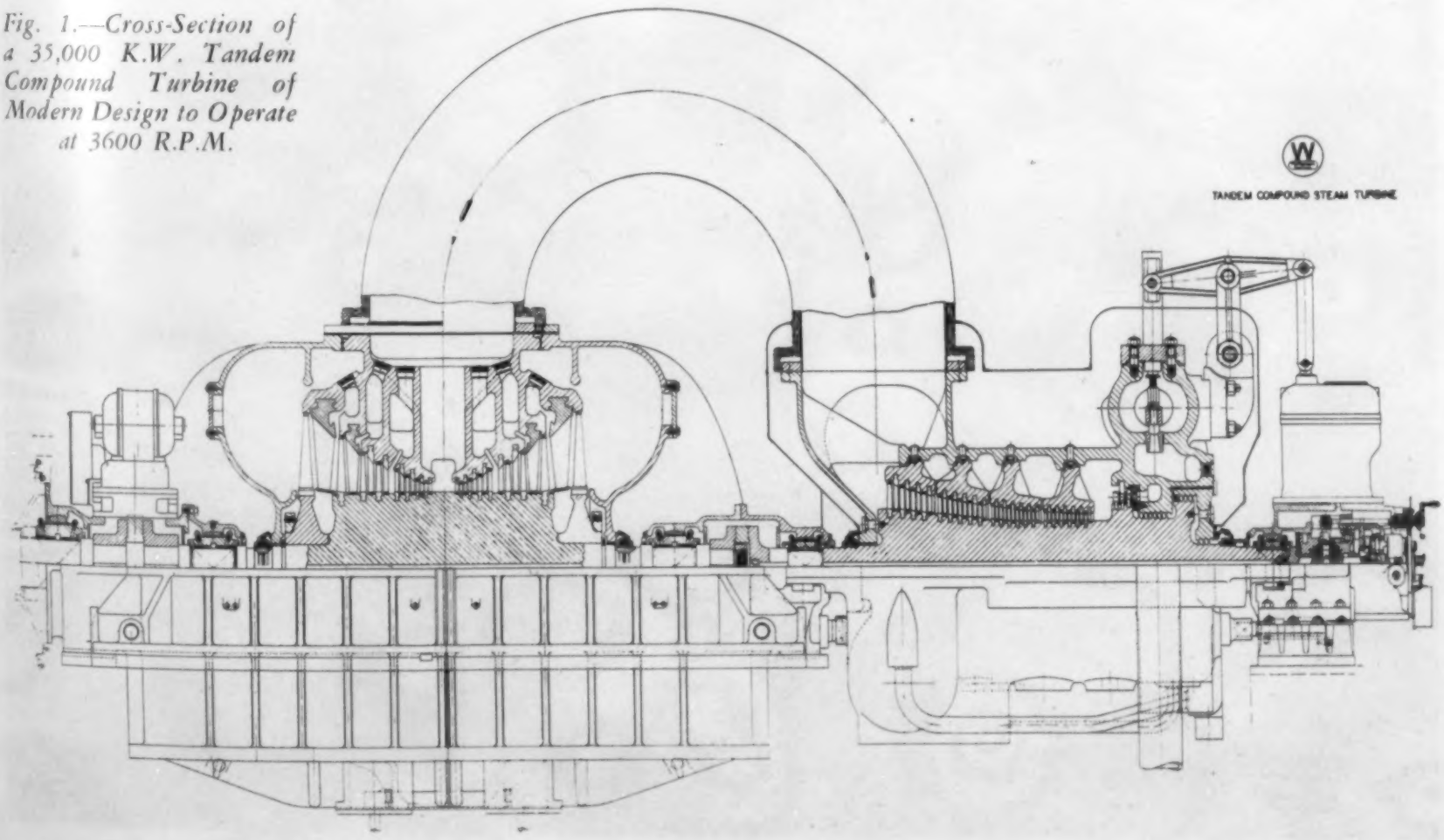


Fig. 1.—Cross-Section of a 35,000 K.W. Tandem Compound Turbine of Modern Design to Operate at 3600 R.P.M.

Naval Review at Spithead in 1897 when Sir Charles Parsons' "Turbinia" reached a speed of 32 knots, the use of the turbine for ship propulsion developed rapidly and now completely dominates the field. As in land service, pressures, temperatures and operating speeds have increased rapidly in recent years.

The statement of 1905 has been more than confirmed in the few years that have passed; truly, the development and adoption of the steam turbine has had a most important part in the development of industry, transportation, and our general civilization.

With the central stations once more enlarging their facilities, and with the widespread installation of turbines in municipal stations and in industrial plants, with the present naval developments and the increase in shipbuilding in general, it is quite natural that considerable interest should be aroused in steam turbines, and, among engineers and metallurgists, an interest in the materials used for their construction.

Materials Used in Turbines

There has been considerable inquiry as to the materials used for turbine rotors, and how they are treated to have them meet the rigid requirements of operation. This interest has come not only from those who are involved directly or indirectly in the purchase or operation of steam turbines, but from those who apparently would consider the use of similar materials and methods for other purposes.

Turbine rotor design has gradually developed from a built-up type using many parts to one employing but a single forged piece.

Originally, reaction or impulse reaction turbine rotors consisted of a hollow shell body, with shaft ends fitted thereto, and a number of separate rings shrunk thereon. There was a gradual reduction in the number of parts, this being especially observed during the period beginning about 1912 to about 1923. At that time, designs were so modified that rarely were more than two pieces used in a rotor, and whenever possible, the rotor consisted of a single forging.

Curtis or Curtis-Rateau designs have long used a central shaft on which are fitted a number of discs, with each disc usually carrying a single row of blades or buckets. This design is still used extensively where temperatures permit, and in low temperature turbines of all types, but in more recent years, there has been a decided trend, as temperatures have advanced, toward the use of a single forging, involving the machining out of the discs to desired shape from the solid forging, and having them an integral part of the shaft.

These general remarks apply as well to central station, industrial and marine turbine practice. It is the purpose of this article to deal primarily with turbine rotor forgings of the one-piece design, although naturally the remarks will apply in some degree to all rotor forgings.

Fig. 2.—A Number of Carbon Steel and Alloy Steel Rotor Forgings Ready for Finish Machining.

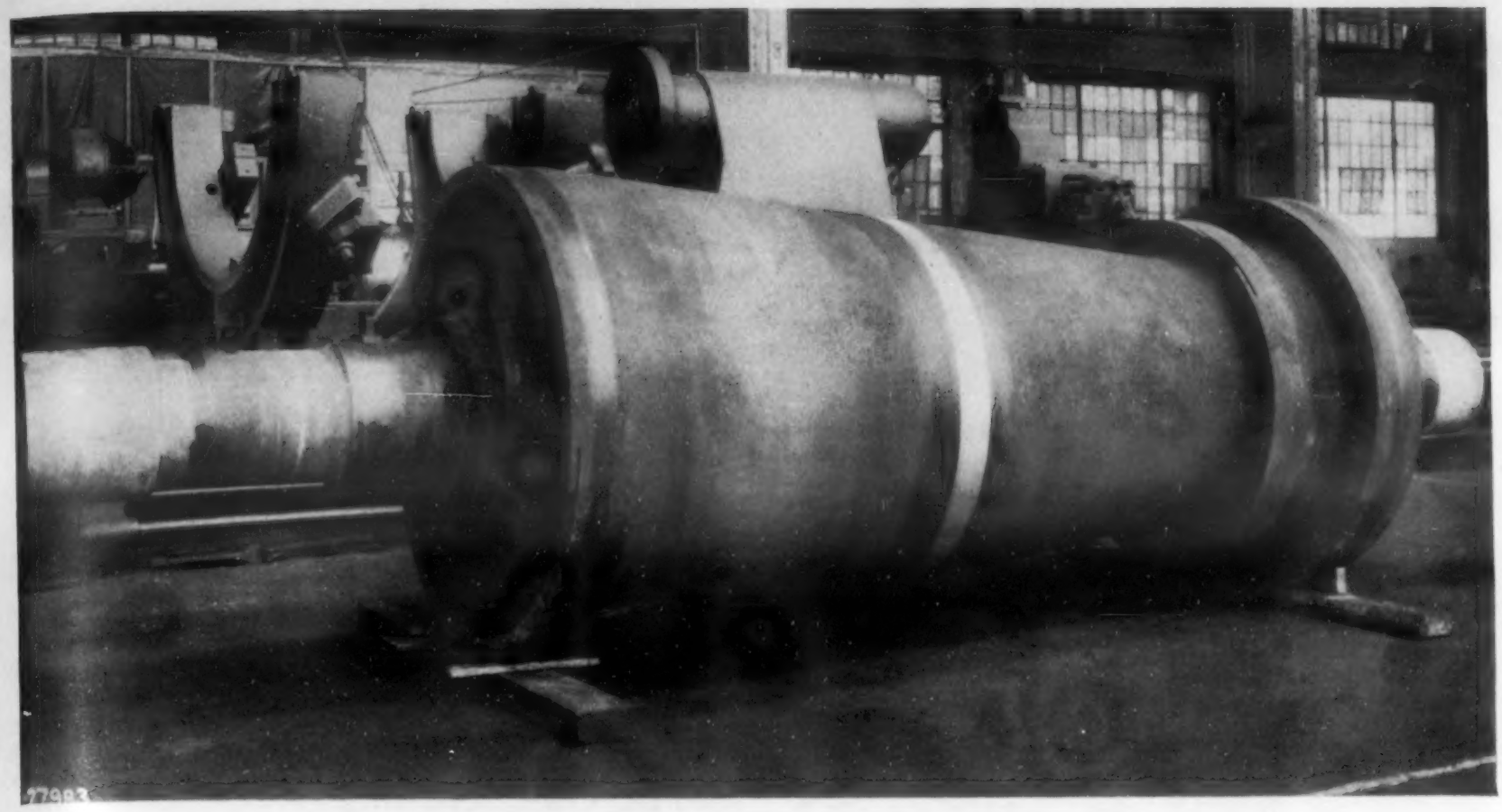


Fig. 3.—A Large Carbon Steel Rotor Forging Weighing 109,600 Lbs.

Fig. 1 shows the cross-section of a 35,000 k.w. tandem compound turbine of modern design, to operate at 3600 r.p.m. It will be noted that the rotor for the high pressure turbine, at the right, is a single forging. The maximum diameter is approximately 31 in., and the rough machined weight 13,800 lbs. It will be noted that the low pressure rotor, at the left, consists of one main forging and two separate discs, one at either end. These could have been forged with the main rotor, but for various engineering and manufacturing reasons have been produced as individual pieces. The main forging has a maximum diameter of 38 in. and the rough machined weight 20,500 lbs.

The turbine rotor must carry the moving blades or buckets, and transmit power to the generator, propeller or other driven member. As speeds of operation, steam pressures and temperatures, blade loads, size and design and operating conditions vary, there is naturally some selection possible as regards material, and heat treatment. There are many requirements and considerations involved, a detailed discussion of which is not intended in this article.

Two Fundamental Considerations

There are, however, two fundamental considerations, and these must control the selection of material and the heat treatment employed:

1. The material must have general physical characteristics to withstand rotation and transmit load.
2. The rotor must be possessed of such general stability as to operate smoothly over many years.

Plain carbon steel was naturally first employed for turbine rotors, and it is still used where design and operating conditions permit. Its service record is very good, indeed we consider it our most reliable material for the purpose.

Advances in operating speeds, temperatures, and blade loads have naturally required the development of alloy steels, in order to meet largely the first of the fundamental considerations given above. This has, however, added greatly to the difficulty of the second consideration.

Nickel steel has long been used, but in more recent years for more severe conditions, the development has largely been in the field of nickel-molybdenum, with the addition in some cases of chromium or vanadium, or both. Typical specifications for carbon, nickel and nickel-molybdenum steel rotor forgings are shown in the Table.

Table of Chemical Composition and Tension Test Requirements of Typical Turbine Rotor Forging Specifications

Chemical Composition: Type	1	2	3	4	5	6
Carbon	0.48 max.	0.45 max.	0.43 max.	0.40 max.	0.43 max.	0.43 max.
Manganese	0.40-0.80	0.40-0.80	0.40-0.80	0.75 max.	0.40-0.80	0.90 max.
Phosphorus	0.04 max.	0.04 max.	0.05 max.	0.04 max.	0.04 max.	0.05 max.
Sulphur	0.045 max.	0.045 max.	0.05 max.	0.04 max.	0.045 max.	0.05 max.
Silicon				0.30 max.		
Nickel		2.75-3.75	2.50 min.	3.25 max.	2.50 min.	2.50 min.
Chromium		0.60 max.	0.30-0.60	1.25 max.	0.60 max.	0.60 max.
Molybdenum			0.20 min.	0.30-0.50	0.30 min.	0.25 min.
Vanadium				0.25 max.	0.25 max.	

Tension Test Requirements: Type	1	2	3	4	5	6
Tensile strength, lbs. per sq. in.	75,000	85,000	90,000	85,000	95,000	100,000
Yield strength, lbs. per sq. in.	40,000	55,000	65,000			80,000
Proof stress, lbs. per sq. in.				60,000	65,000	
Elongation in 2 in.	20.0	20.0	18.0	15.0	18.0	18.0
Red. of area, per cent.	35.0	40.0	40.0	24.0	35.0	40.0

The tensile properties shown above are for tangential test specimens for Types 1-2-3-5-6 and for radial specimens for Type 4, all located at greater than half radius of the forging. Longitudinal specimens require higher percentages of elongation and reduction of area than those shown, and, when tangential or radial specimens are located at less than half radius, slightly lowered values of elongation and reduction of area are allowed.

Such analyses and required physical properties are so arranged that the properties may be readily met by normalizing and drawing, and the first of our fundamental considerations is taken care of.

For many years, the Westinghouse company more or less assumed responsibility for the second consideration, and required the supplier to merely meet the specified physical properties. The forgings were then carefully rough

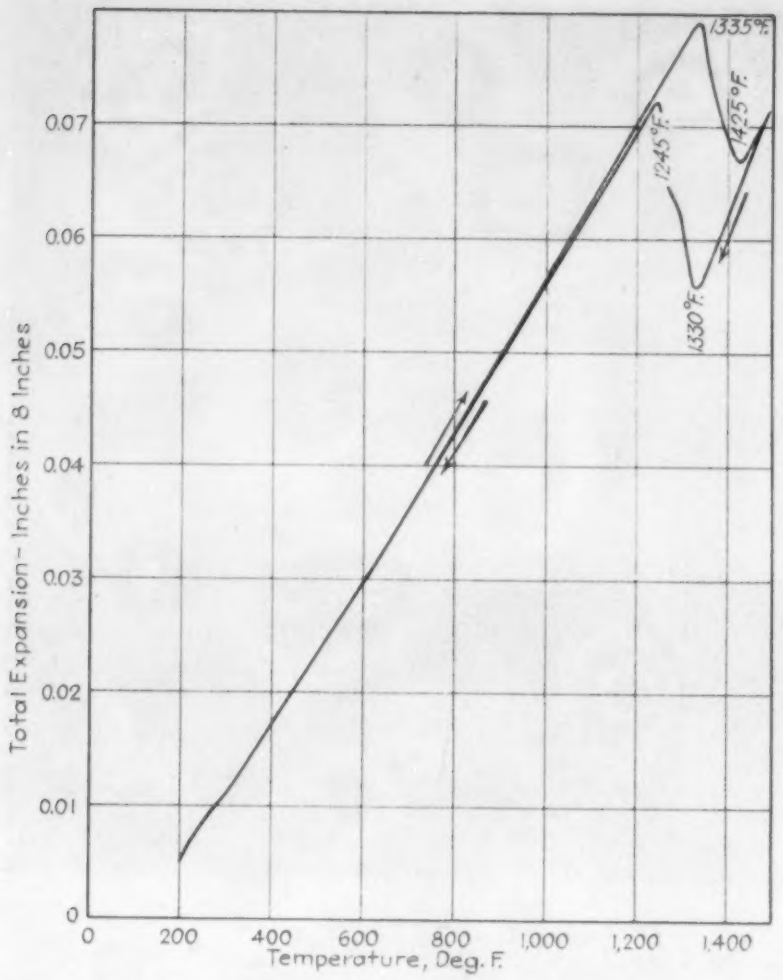


Fig. 4.—Critical Ranges Determined on a Carbon Steel Rotor Forging.

machined more closely to finished size and shape, and given a long stress-relieving treatment, usually in round, vertical furnaces, if possible hanging the forgings in the furnace. Later, it became apparent that the second fundamental consideration, the matter of stability, should be dealt with from the very beginning, and the heat treatment to give desired properties, and the heat treatment to give desired stability, should be coordinated, and carried out entirely by the forging manufacturer.

Heat Treatment of Carbon Forgings

For carbon steel forgings, the Westinghouse company specifies heat treatment as follows:

> (a) Forgings of 40 in. diameter and larger shall be treated as follows: When the forging is completed, and without permitting it to become cold, it shall be taken to the treatment furnace and uniformly reheated to a temperature sufficiently above the upper critical range to break up the ingot structure, held the necessary length of time and then withdrawn from the furnace and air cooled under closely controlled conditions, protected from moisture. Upon being cooled to a black state, it shall be reheated to a low annealing temperature, held the necessary length of time and uniformly cooled. The forging shall then be preliminary rough machined all over, including the rough boring of the axial exploration hole. The forging shall then be charged into a cold furnace and reheated to a temperature above the upper critical range to refine the grain, held the necessary length of time, and withdrawn from the furnace and air cooled under closely controlled conditions, protected from moisture. Upon being cooled to a black state, it shall be reheated to a low annealing temperature, held the necessary length of time and uniformly cooled. The forging shall then be rough machined to the dimensions of the purchaser's forging drawing, after which it shall again be charged into a cold furnace, reheated to a temperature of not less than 1050 deg. F., held for a sufficient length of time and cooled slowly in the furnace. No further machining other than cutting off test specimens and finish boring of axial exploration hole is to be performed after this final annealing.
>
> (b) Forgings less than 40 in. diameter may be treated in the same manner as outlined above; or the sequence of heating and machining operations may be varied depending on the size and shape of the forging, but in any event, the forging shall be heated twice to a temperature above the upper critical range and air or furnace cooled, and it shall receive a final low temperature annealing at a temperature of not less than 1050 deg. F. and slowly cooled in the furnace after all rough machining has been completed.

In reality, a typical treatment would be as follows, with a carbon content of 0.42 per cent:

> 1600 deg. F.—hold 30 hrs.—air cool to black
> 1260 deg. F.—hold 30 hrs.—furnace cool
> Rough machine
> 1480 deg. F.—hold 27 hrs.—air cool to black
> 1200 deg. F.—hold 30 hrs.—furnace cool
> Machine to specified dimensions
> 1050 deg. F.—hold 48 hrs.—furnace cool.

No Liquid Quenching

Liquid quenching is not permitted. In Europe, it has been the practice to oil quench large rotor forgings, but American producers and consumers are agreed against such practice. Discs of comparatively thin and uniform section have been quenched at times, but by altering the chemical composition, it has been found possible to secure the desired properties without resorting to quenching.

Fig. 2 shows a number of carbon steel and alloy steel rotor forgings ready for finish machining. The variety of shapes and sections is well illustrated. Fig. 3 shows a large carbon steel rotor forging, weighing 109,600 lbs. The largest diameter is 62 in., and the overall length is 20 ft. 7 in.

It is believed that a consideration of the masses, and variable sections involved, will convince that liquid quenching is a practice to be avoided.

The specified treatment for alloy steel forgings is the same as that specified for carbon steel forgings over 40 in. in diameter; in other words at least two normalizing and drawing heats, and a final stress relieving treatment. In some cases, it is desirable in the first stage to normalize twice before the first drawback. The temperatures and times used must of course be adjusted to the composition used.

Use of Alloy Steel

Alloy steel, as stated above, largely becomes necessary under the first fundamental consideration, that is to provide physical properties ample to support the loads involved. In some cases, high temperature may be the controlling factor; in other cases, it is purely by reason of high loads. For example, in a low pressure rotor, such as the one shown in Fig. 1, alloy steel is used for the rotor because of the long blades and the high speeds encountered. In the case of the high pressure rotor in Fig. 1, the use of the alloy steel rotor is more by reason of the high temperature encountered, in this case, 850 deg. F.

It was stated above that the use of alloy steel adds greatly

to the difficulty of the second consideration, the feature of stability. The release of internal stresses in turbine rotor forgings is imperative, if smooth running is to be secured. Stress relieving is purely a matter of relaxation, accomplished by heating a material to a sufficiently high temperature as to permit the relaxation of those stresses in the time period used. Stress relieving, in the author's opinion, involves three factors: Temperature, time, and the amount or degree of stress involved. High stresses are more quickly relieved than low stresses; and the higher the temperature, the more quickly stresses are removed. Stresses of low degree, that in years past because of lower temperatures of operation did not "come out" and interfere with service, now become serious with the higher operating temperatures.

Creep and relaxation are closely related, and involve the same general considerations. It will be readily appreciated that, when we devise an alloy steel to give improved strength and creep resistance at high temperatures, at the same time we make it more difficult to bring about relaxation or relief of internal stresses. Longer time periods naturally become necessary.

Further, the temperature that can be utilized for stress relieving is restricted by our first consideration; the desired physical characteristics must be retained.

The use of nickel as the main alloying element was probably a natural one. Producers and users alike had a background of experience with it, especially when heavy masses were involved. The first need for alloy steels was largely for increased physical properties, at moderate temperatures. It readily gave the desired properties.

We know, however, that the addition of nickel to steel lowers the critical ranges, both during heating and cooling.

Critical Ranges

Fig. 4 shows the critical ranges determined on a carbon steel rotor forging, and Fig. 5 on a Ni-Cr-Mo-V rotor forging. Actual analyses were as follows:

	Carbon Steel	*Ni-Cr-Mo-V Steel*
Carbon	0.42	0.27
Manganese	0.71	0.56
Phosphorus	0.043	0.015
Sulphur	0.033	0.019
Silicon	0.235	0.176
Nickel	nil	2.70
Chromium	0.10	0.10
Vanadium	nil	0.094
Molybdenum	nil	0.31

Now it is recognized that these are laboratory determinations on small specimens cut from the rotor, and that the rate of cooling has a very considerable effect upon the position of the Ar ranges. However, the laboratory specimens were slow cooled in the furnace, and the large forgings were air cooled through the critical ranges, and it is believed the curves show in a fair way, the general position of the ranges.

In air cooling such forgings as shown in Figs. 2 and 3, it will be appreciated that the outer portions, end faces, shaft portions, etc., must cool more rapidly than inside portions, and will progressively pass through the critical ranges while other portions lying underneath are as yet above the critical ranges.

We will note in the case of carbon steel, Fig. 4, that the range extends from 1330 deg. F. to 1245 deg. F. Carbon steel at such temperatures is quite plastic and the changes in

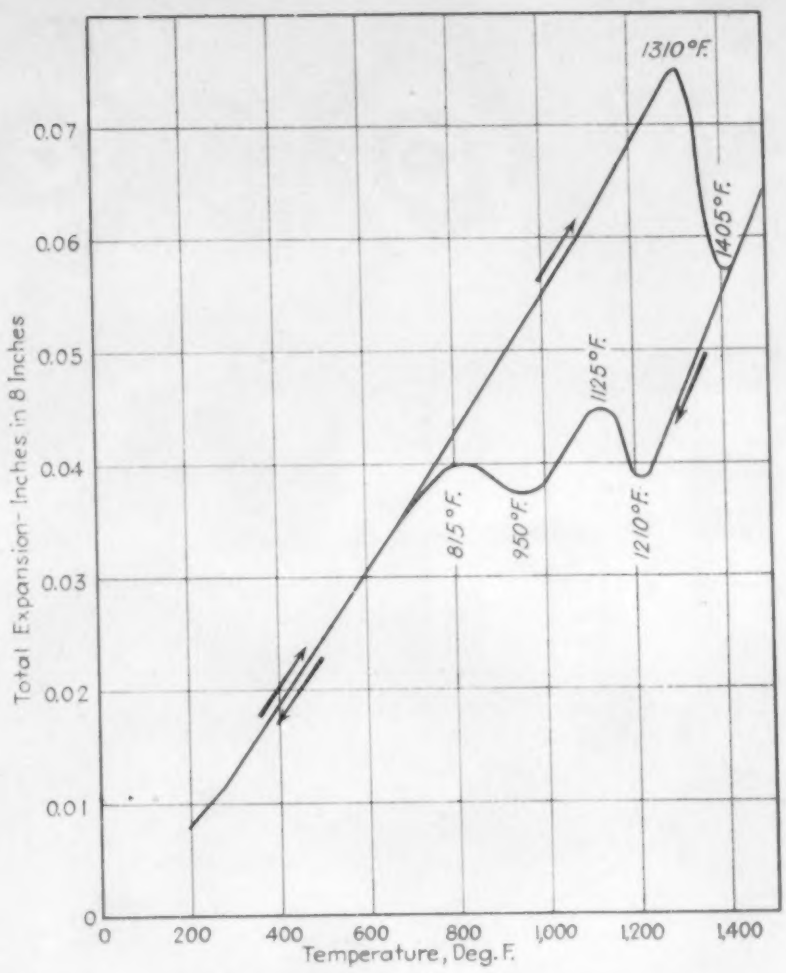


Fig. 5.—Critical Ranges on a Ni-Cr-Mo-V Rotor Forging.

volume can be accommodated without the setting-up of undue stresses. Such internal stresses as are set up can be relieved by a reasonable length of time in the final draw and stress relieving treatments.

We will note, however, in the case of the alloy steel, Fig. 5, that the range is much lower, and extends as low as 815 deg. F. Considering the higher strength characteristics of such a steel over the temperature ranges where volume changes are shown, it will be appreciated that quite high internal stresses may be set up, which can only be removed by longer time periods in the final draw and final stress relieving treatments. The author, therefore, feels that long final anneals of the order of 50 hrs. are necessary for best results.

Our experience going back many years indicates that round vertical furnaces, in which the rotor may be supported or hung with the axis vertical, are to be preferred for these final heats.

A Need Stressed

Plainly there is need for a steel that can be used for turbine rotor forgings that will give the desired properties under the first consideration, and that will have critical ranges sufficiently high as to assure that volume changes will take place at those temperatures where the metal is quite plastic. Much thought is being devoted to this problem.

The suitability of turbine rotors under the first consideration is judged by analyses, tension tests, the structure, sulphur printing, magnetic examination, and internal bore examination; the suitability under the second consideration by the so-called heat indication test at the place of manufacture and the shop running tests in the turbine manufacturer's plant.

Courtesy: Ford Motor Co.

Tapping Pig Iron from a Blast Furnace

METALS AND ALLOYS USED IN

DIESEL LOCOMOTIVE CABS

by Edwin F. Cone

THE MANUFACTURE OF DIESEL LOCOMOTIVES for railroads is a comparatively new industry. It has already grown to fairly large proportions. The problems involved in the construction of these units have been many, particularly as to the selection of metals and alloys. Many of these problems have been solved, for the present at least, and others are still being studied.

It is the object of this article to put before the reader some of the interesting facts about the steels which go into the construction of certain types of Diesel locomotives, why they are selected and how they are handled. By locomotive is understood the cab or large framework which houses the engine, and not the engine itself. The facts are based on the experience of the Electro-Motive Corporation, La-Grange, Ill., a subsidiary of General Motors Corporation whose valued cooperation is acknowledged.

This company produces in its modern plant, Diesel switching locomotives and Diesel high-speed passenger locomotives. The power plant or engine is furnished by the Winton Co., Cleveland, another subsidiary of General Motors. There is a distinct difference between these two types of locomotives or cabs: Low weight is an important factor in passenger locomotives, but weight is added on switching locomotives in order to get the required tractive effort. To the extent that these differ, as stated, so do they differ as to the steels needed in them. Therefore this article will be divided into two parts—a description of the passenger and then the switching locomotives. In each case the portion which houses the Diesel engine—the superstructure—is treated first, and then the trucks, including the wheels and axles, which carry the cab.

Diesel Passenger Locomotives

FROM the point of view of the metal which is incorporated in the Diesel passenger or high speed locomotives, this unit is doubtless more interesting than is the switching locomotive because more alloy steels are used. A problem involved in both types, however, is the incorporation of the proper weight on the super and under structures to support the weight of the Diesel engine itself. And with this is involved the consideration of strength, particularly because the passenger unit must travel at a very high speed. The engines are 1800 H.P. and the locomotives travel at a maximum of 100 to 120 miles per hour.

In the high-speed locomotive, weight is naturally a primary consideration, but this must be kept down so far as possible in order to insure a quick get-away. Therefore

One of the Completed High-Speed Diesel-Electric Locomotives.

A Typical Diesel-Electric Switching Locomotive.

strength is vital, combined with high impact resistance. In the design and construction of these locomotives therefore, there are involved lightness with enough weight; steels of sufficient strength to insure lightness and not excessive weight; the absence of, or the counteracting of stresses from, welding; and impact resistance.

Superstructure — All Welded

The framework of the superstructure of the passenger locomotive is made of two types of steel—one for those parts that are load or stress-bearing and the other for those that do not carry any particular load. The entire superstructure is welded. For the stress or load-bearing parts, a manganese-molybdenum steel is used exclusively, and for the other a plain carbon steel, S.A.E. 1020.

The Low-Alloy Molybdenum Steel

For the load or stress bearing metal, the company has selected a low-alloy, high elastic manganese-molybdenum steel. Rather it should be stated that it is a modified pearlitic Mn-Mo steel, the manganese averaging 0.90 to 1.00 per cent. It is a basic open-hearth product. The composition and properties of a typical steel are given in the Table. This steel is used as plates up to 2 in. thick, as sheets of various gages, and as shapes required by the various parts for which intended.

Some of the reasons given by the company for using this steel are as follows:

1. Its high yield strength and rather high tensile strength.
2. Its excellent forming properties, particularly cold bending.
3. No cracking in shearing.
4. Good endurance properties.
5. Good impact properties at low temperatures.
6. Weldability, highly satisfactory.

Front View of All-Welded Frame Work of High-Speed Diesel-Electric Locomotive Prepared for Loading Tests.

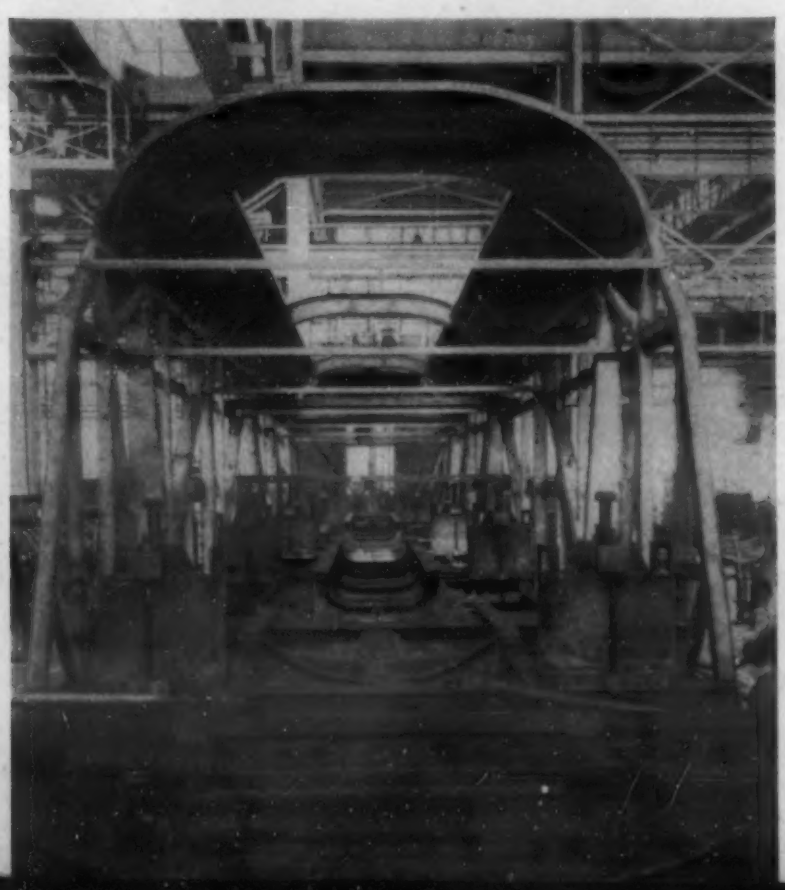
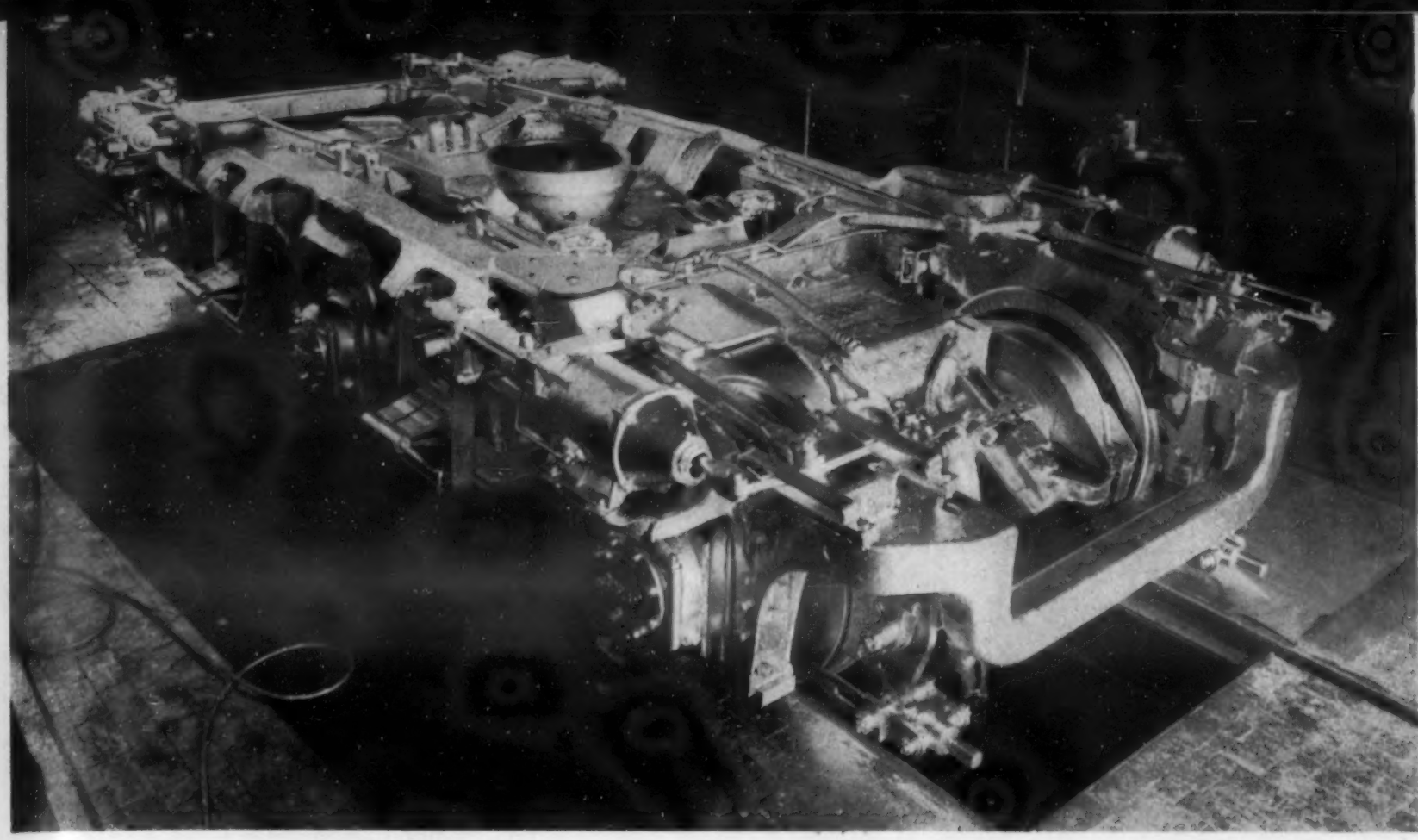


Table of a Typical Composition and Properties of the Mn-Mo Steel compared with Plain Carbon. (Per cent)

	Mn-Mo	Plain Carbon
Composition:		
Carbon	0.13	0.16
Manganese	0.91	0.44
Silicon	0.17	0.01
Phosphorus	0.016	0.012
Sulphur	0.017	0.021
Molybdenum	0.51	...
Copper	0.08*	0.04*
Nickel	0.07*	...
Chromium	0.04*	...
* Residual.		
Physical Properties (As Rolled):		
Tensile strength, p.s.i.	83,280	62,650
Yield point, p.s.i.	63,540	39,800
Elongation in 8 in., %	23.5	37.6
Red. of area, %	56.6	58.9
Brinell, No.	149	121
Bend, deg.	180	180

These reasons are founded on extensive tests based on a careful survey of weld samples and comparisons made with other commercial materials of the above characteristics. The consideration of impact properties at low temperatures is brought into the picture because the locomotives must often travel in cold climates at high speeds. Wherever possible, welded parts are stress relieved in a furnace, later described. Naturally, the whole structure can not be stress relieved, but the beams and floor of the cab can be, and are.

As stated above, this entire superstructure in which these

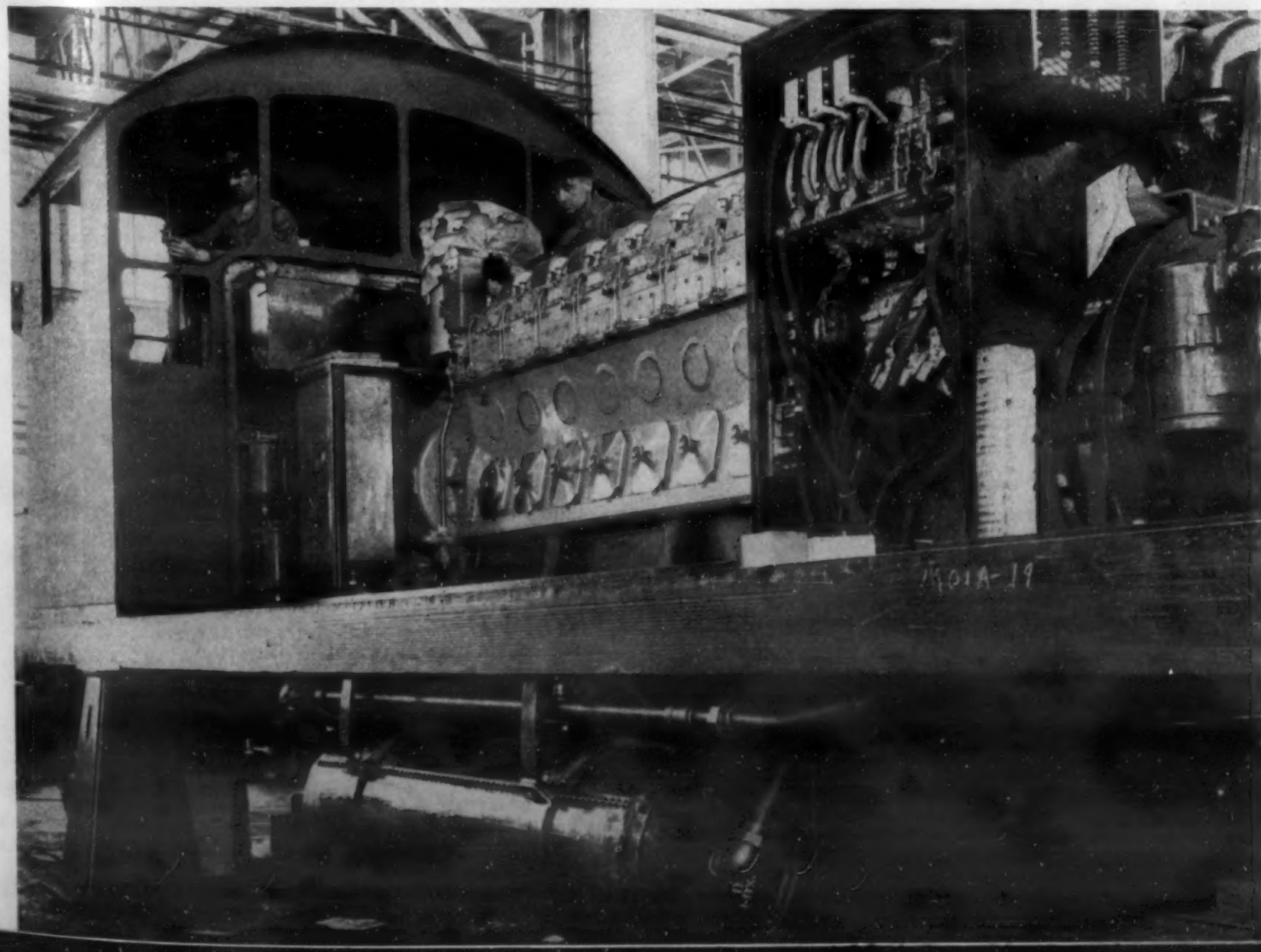


Truck Assembly of Modern High-Speed Diesel-Electric Locomotive.

two steels are employed is welded. In the welding of the Mn-Mo steel, welds are made by electrodes which approach in composition the parent metal in all cases. Practically all known methods of welding, automatic and manual, are used.

The underframe structure or high speed Diesel electric locomotive is a series of beams of welded Mn-Mo steel. A description of this is difficult but, by consulting the illustrations, some conception of its design is possible. After the framework is completed and such stress relieving as is necessary and possible has been taken care of, the skeleton at some stage in the construction is covered. Here also, two types of steel are used. If the covering is not to be painted, stainless steel is employed. If it is to be painted,

The Cast Steel Foundation or Underframe of a Switching Locomotive. The thick plate which is welded on top of the casting, as described, can be detected.



One of the Many Welding Operations Used on Both Types of Locomotives. This is a welding operation on a switching locomotive.

as per specifications, sealed galvanealed ply-metal panel is used. In some instances a ply-metal with stainless on the outside and galvaneal metal inside, is the rule.

The roof is frequently covered with stainless steel, plug welded by a special process. In other cases a low-alloy, high elastic steel is specified and protected by proper painting. The importance of good impact properties—40 ft. lbs. or over at ordinary temperatures—with high strength and a low weight ratio is highly stressed in the selection of this sheet material.

The Understructure

The trucks underneath this welded superstructure are of conventional design into which alloy steels also enter. This truck frame and bolster is an intricate and interesting one-piece casting of 2.25 per cent nickel steel, double annealed and drawn. Its properties are approximately as follows: Tensile strength 86,500 and elastic limit 52,000 lbs. per sq. in.; elongation 28 per cent in 2 in., and reduction of area 56 per cent.

The wheels are not standardized as to composition. Plain carbon rolled steel wheels are seldom used, oil quenched and drawn, as well as also a water-toughened rolled steel wheel, rim treated. A molybdenum steel rolled wheel is employed in some cases. The company has also experimented with cast steel wheels, subsequntly rolled and heat treated, but no decision has yet been finally made as to composition and heat treatment. Quite obviously these wheels have to stand much punishment at the high speeds employed.

A forged steel axle is used, standardized for both the highspeed and switching locomotives. It is a high carbon steel of approximately the following properties: C 0.54; Mn 0.72; Si 0.22; P 0.017; S 0.026 per cent with a tensile strength of 89,420, and an elastic limit of 51,950 lbs. per sq. in., and an elongation of 27 per cent in 2 in. and a reduction of area of 46 per cent.

The inspection of these axles is severe. Duplicate test bars are employed and etch tests are made of cross sections in order to minimize the possibility of fatigue failures. Each axle is ground all over and given a careful magnaflux test. Any axle is rejected which shows even the most minute cracks, surface seams or ghost lines.

The equalizers for the trucks, standardized for both types of locomotives, are high carbon forgings, double normalized, followed by drawing treatment, with a tensile strength of 92,100 and an elastic limit of 54,500 lbs. per sq. in., and an elongation of 25.0 per cent in 2 in. and a reduction of area of 44 per cent. Its Brinell is 116 to 134, and its impact value at room temperature is 37.5 ft. lbs. (Charpy). At low temperatures this value is also satisfactory.

As a safety precaution, drop tests, using a 1640-lb. tup, are made with heights of drop up to 50 ft. 5 in. with resulting deflections of 7.36 in. without producing defects of a visible nature. Springs for the trucks are plain carbon steel, heat treated to specified low deflection characteristics.

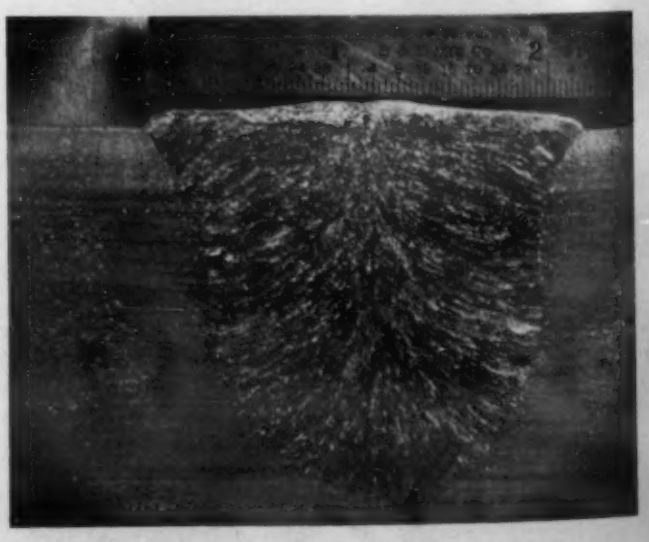
An important point in the building of these locomotives is the fact that load deflection tests are made with extreme precision and care on every new design. Such load deflection tests require elaborate and extensive apparatus, and two to three days to complete in the case of the superstructure of a large locomotive.

Diesel Switching Locomotives

IN designing the Diesel switching locomotives, ample weight is primarily the consideration. Lightness is not so essential as in the case of the high-speed passenger unit, nor is strength combined with lightness so much a factor. The switching locomotives, which are standardized at 600 and 900 horsepower do not of course, travel at high speeds.

The Superstructure

A distinguishing feature of this type is that it employs a heavy underframe, made in two different ways: it is either a large cast steel rectangular slab on top of which a steel



Micrograph of One of the Welds Used in the Construction of Diesel-Electric Locomotives.

plate, about ½ to ¾ in. thick is welded; or it is of welded construction into which plates of plain carbon steel up to 4 inches thick enter.

These cast underframes weigh up to 52,000 to 53,000 lbs. each. If the steel casting is the main portion, it is a plain carbon steel of about 0.18 to 0.20 per cent carbon with a tensile strength of about 61,000 to 62,000 lbs. per sq. in. One of the illustrations shows this heavy underframe steel casting with the steel plate welded thereon. If the underframe is welded up of heavy steel plates, fillet welded by a special process, plain carbon steel is here also employed. Such an underframe is always stress relieved as described later. The welding of these large underframes by the automatic process is highly interesting and spectacular.

In building the switching locomotives, the superstructure is similar in a few respects to that of the high speed unit except that plain carbon steel is employed. It also is completely welded. This structure varies in length from 47 ft. to 58 ft. with a height of 13 ft. 11 in. and a width of 9 ft. 10 in.

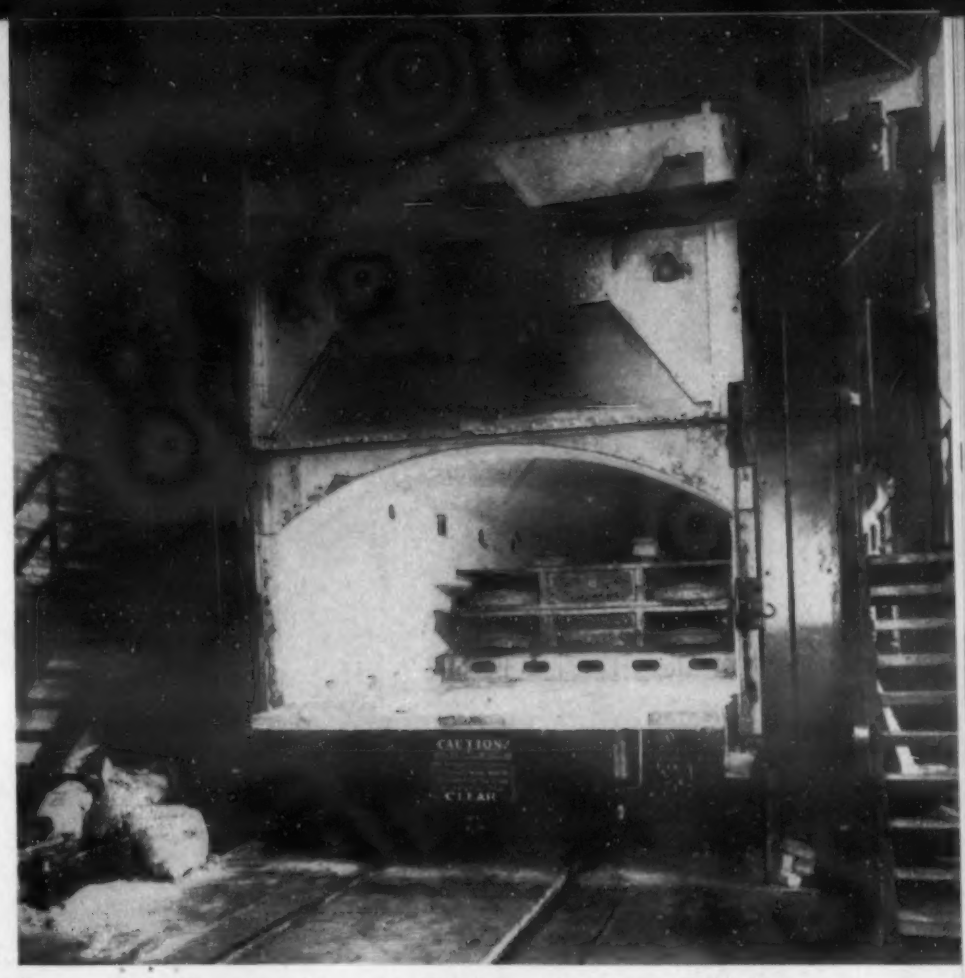
The Understructure

In the 4-wheel trucks for the switching locomotives, the side frames and bolsters are not separate castings, plain carbon steel being the rule with a carbon content of around 0.18 to 0.20 per cent and a manganese of about 0.85 per cent. The average tensile strength of the truck frame is around 73,000 lbs. per sq. in. and the weight is close to 5,700 lbs. each.

The wheels in this case are rolled steel with a carbon of about 0.76 per cent with the manganese approximating 0.77 per cent. They are either oil quenched and drawn or rim toughened by a special process. In most cases the customer is given the type desired. As to axles and equalizers, the same steels are used here as in the passenger locomotives described earlier.

Stress Relieving Furnace

The heavy welded underframes of the switching locomotives and certain of the welded portions of the passenger or high-speed units are always stress relieved. This is accomplished in a specially designed furnace, fired by gas



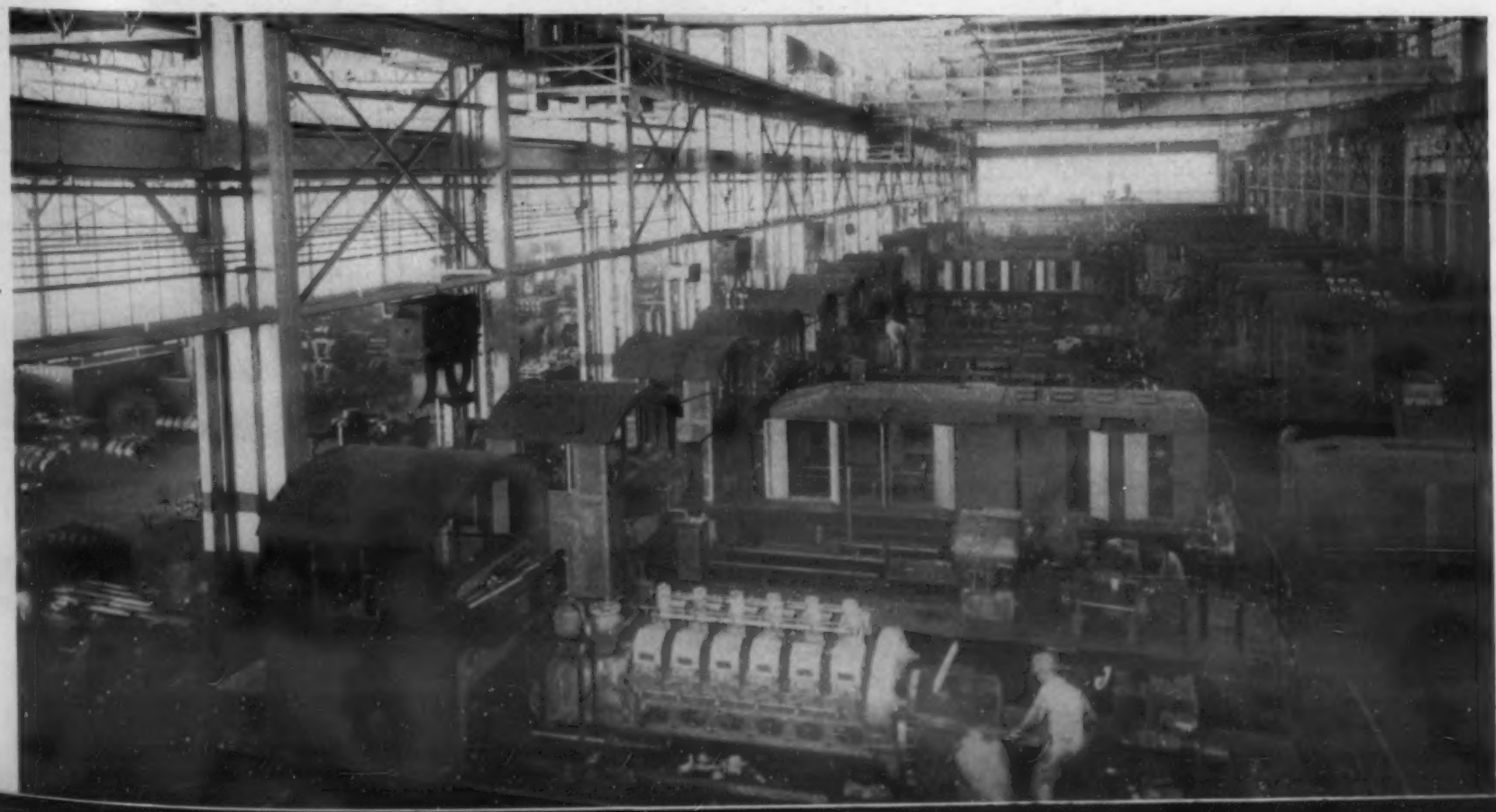
Large Heat-Treating Furnace Used for the Stress Relieving of Welded Underframes of Modern Diesel-Electric Switching Locomotives. Capacity is a charge of 100 tons.

under high pressure, with pyrometric and draft control.

The furnace is 74 ft. long, 13 ft. wide and 9 ft. high effective clearance. Charges up to 120 tons are used. For stress relieving the material is heated up to 1200 or 1250 deg. F. and always cooled in the furnace.

Two facts stand out prominently from this recital—the extensive use of welding and the dependence on alloy steels. Advances in the art of welding—particularly the automatic process—have made it possible to depend on this method of construction in solving certain problems of construction and in securing certain reliable and desired results. The development of the low-alloy, high elastic steels has also made possible the building of structures where lightness in weight is combined with adequate strength and resistance to impact, together with satisfactory welding properties. Doubtless these developments are forerunners of still further interesting ones to come.

General View of a Portion of the Large Plant. Here switching locomotives are being assembled.



Courtesy: Ford Motor Co.

Electric Arc Welders in the Ford Rouge Plant Power House

Internal Stresses in Welds—

THEIR CAUSE AND EFFECT

by A. B. Kinzel

Chief Metallurgist,
Union Carbide & Carbon Research Laboratories,
New York.

THE SUBJECT OF INTERNAL STRESSES in welded structures has been the source of a great deal of speculation and conversation in the past few years. Opinions on this subject differ radically, from the simple view that such internal stresses are non-existent or at any rate inconsequential, to the other simple extreme that internal stresses in welded structures are potentially so serious that all welded structures should be stress-relieved. To those who have been following the art and science of welding it is obvious that neither of these simple views is justified, that the matter is far from simple and that as yet it appears to be too complex to warrant generalization.

Proof of Internal Stresses

That internal stresses are produced to a greater or lesser degree in any welding operation can be readily proved by anyone who wishes to take the trouble to cut a welded plate into a number of portions and note the accompanying change in dimension. It is true that a similar change in dimension—frequently of the same order of magnitude—also occurs when this test is applied to hot-rolled products, but little is known about the internal stress distribution in the two cases and it is probable that there is a marked difference in that the stresses existing in the welded structure are much more complex, generally less evenly distributed, and subject to highly local concentrations. Thus, the argument that internal stresses in welded structures are of no consequence because similar stresses occur in hot-rolled products has little weight.

Again, it is pointed out that cold-rolled products carry very high internal stresses. Bridge wire is frequently cited as a case in point, and, based on the analogy with bridge wire, the argument proceeds to the conclusion that internal stresses in welded structures are not harmful. Again, the reasoning is weak, in that the internal stresses in the bridge wire are parallel to the externally applied stress and single dimensional in character. This naturally leads to consideration of the causes and the nature of the internal stresses produced in welding.

Upsetting Action

In joining two plates of appreciable size by the fusion welding process, the edges to be joined are heated to the solidus temperature of the metal in question. A temperature gradient runs from this point to the cold plate, and the normal expansion which would take place in the high temperature zone is restrained by the colder metal immediately adjacent thereto. This restraint results in an upsetting action whereby the linear expansion of the hot zone is converted to bulk expansion, with actual thickening of the plate of this zone.

As is well known, this upsetting action is not reversed on cooling. In fact, it is probable that it continues to take place during a portion of the cooling cycle. If the time-temperature conditions on heating and the time at maximum temperature were sufficient so that the metal at moderately elevated temperatures would creep to such an extent that it was completely free from elastic stress, and if the time-temperature conditions were the same on cooling as on heating, we might expect the reverse of the upsetting action on cooling. In steel, however, even the postulated conditions would not be sufficient because the allotropic transformation on rapid cooling takes place at a much lower temperature than on heating, and both the elastic and plastic characteristics of the material differ in the two allotropic states. Moreover, in the welding of steel plate the other postulated conditions are far from being fulfilled. With normal speeds of welding, the rate of heating and the time at temperature do not allow the upsetting action even to approach completion so that it is still going on during some of the cooling, and the allotropic transformation taking place at a rather low temperature further complicates conditions.

The accompanying curves, Figs. 1 to 4, taken from T. P. 597, AIM&ME., February, 1935, by A. B. Kinzel, are illustrative of the conditions for gas welding. They were taken during the production of a 36-in. weld in ½-in. plate. Similar curves for electric welded material show much steeper gradients, so that the condition is still further exaggerated. Obviously, the magnitude of the internal stress produced in this manner will be a function of the length of the weld up to some limiting length, after which it will be practically constant. This is due to the fact that the end of the weld is a free surface and there can be no normal internal stress at such a surface. This end effect is transferred in some degree to the adjacent material.

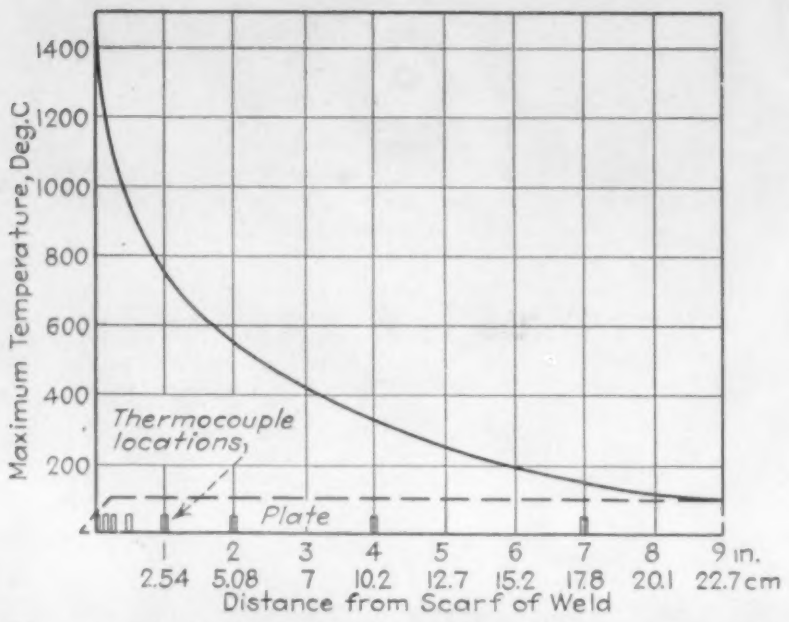


Fig. 1.—Maximum Temperature Reached at Various Distances from a Gas Welded Seam in a 1/2-in. Steel Plate.

Quantitative Aspects

While no published work seems to be available on the quantitative aspects of this end effect, it is generally recognized that free welds up to about 6 in. in length in material of thickness usually encountered are reasonably free from stress parallel to the weld, and that an internal stress condition approaching the maximum appears if the weld is some 2 or 3 ft. long, the internal stress remaining more or less constant as the weld exceeds this length. Thus, other things being equal, the intensity of the internal stresses for any given length and thickness of weld will depend largely on the thermal gradient. The steeper this gradient, the greater the differential length change between the adjacent zones and the greater the intensity of the internal stresses.

The well-known surface tension phenomenon whereby a cube of steel will assume spherical shape when heated and cooled often enough has been mentioned in the production of internal stresses, but it would seem that this is quantitatively inconsequential as compared to the phenomenon above described.

It is to be particularly noted in connection with the above argument that the internal stresses in externally unrestrained members are produced in a direction parallel to the weld and occur in the heat-affected zone immediately adjacent thereto. Whether or not they are to be eliminated by processing before a welded structure is put into service depends largely on their magnitude. All of the above pertains to the welding of externally non-restrained structures, such as plates which are free to move as a whole and tubing, one end of which is free.

Occasionally it is necessary to weld members which are externally restrained, such as two plates, both of which are rigidly affixed to some other part of a larger structure, or tie rods in aircraft fuselages and the like. The problem here is essentially different from that previously discussed in that, due to the linear expansion at right angles to the weld on heating, tensile forces are set up across the weld when the material contracts from the welding temperature. In this instance the temperature gradient in the lower temperature ranges plays a major role. After the weld is completely solidified no tensile forces of consequence are produced until all of the material is at a temperature below approximately 500 deg. C, as any material in this range will promptly undergo plastic deformation and relieve tensile forces. Thus, the magnitude of the internal stresses produced under these conditions will be an inverse function of the amount of material in the so-called stress-relieving range

Fig. 2.—Maximum Temperature Reached at Short Distances from a Gas Welded Seam in a 1/2-in. Steel Plate.

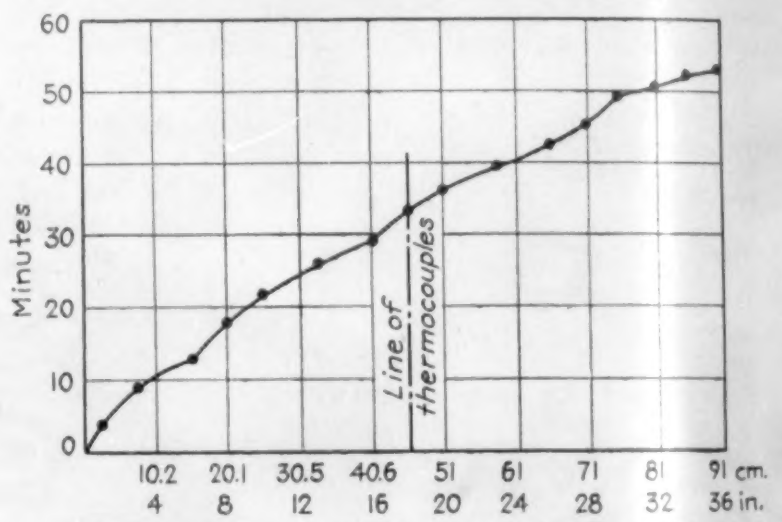


Fig. 3.—Speed of Welding in 1/2-in. Test Plate.

as the material cools. Once again the matter of temperature gradient is involved, in that the steeper the gradient the less material available for platsic deformation and stress relief in the later portion of the cooling cycle. It will be seen then that the problem differs materially from that of the larger, externally-unrestrained structure in which internal stresses are produced parallel to and not across the weld.

Internal Stresses Parallel to Applied Stresses

That innumerable welded structures containing internal stresses of a relatively high order of magnitude have given excellent service over many years is well known to all. This raises the question as to why internal stresses presumably have been harmful in a very small percentage of welded structures. It is probable that the answer to this question involves the mechanism by which internal stresses promote failure and the natural means of their relief or elimination.

In the opinion of many, internal stresses which are parallel to the direction of applied stresses are of no moment in the usual, ductile structural steels. The applied stresses added to the internal stress result in a local strain exceeding that of the yield strength. The material, boiler plate or the

like, yields accordingly, this strain being accomplished without increase of stress. The net result is material which has been locally cold worked to such a small degree as to be negligible, the internal stress being largely eliminated in the operation.

For example, a load of 25,000 lbs. per sq. in., is applied to a bar, the center of which for one reason or another is in internal tension amounting to 20,000 lbs. per sq. in. The yield strength of the bar is assumed to be 30,000 lbs. per sq. in. The cumulative effect of the internal stress and applied load does not result in a stress equal to their sum—45,000 lbs. per sq. in.—but in the yield strength stress, 30,000 lbs. per sq. in., the other 15,000 lbs. per sq. in. being absorbed in a strain of about 0.0005 in. per inch, which occurs as permanent plastic deformation. On removal of the external load the stress drops 25,000 lbs. per sq. in. from the 30,000 lbs. per sq. in. level, leaving an internal stress of 5,000 lbs. per sq. in. It is realized that the above is a somewhat simplified version of the actual quantitative state of affairs, which neglects the reaction of the counterbalancing compressive stresses in the outer portion of the bar, but we choose to neglect this in the interest of clarity.

It will be apparent from the above that the internal stress parallel to the applied stress does not tend to cause failure of the material once the weld has been completed, and to all intents and purposes may be considered as inconsequential.

Internal Stresses at Right Angles to Applied Stresses

A very different state of affairs exists, however, if the internal stresses are at right angles to the applied stress. Consider a cube to which tension is applied on all six faces. (See Figs. 5 and 6.) Obviously, except for a minute elastic volume change which can be neglected for purposes of this argument, there can be no deformation. The yield strength is the equivalent of the ultimate strength, and brittle failure results. Under elastic conditions any applied stress has components at right angles equivalent to this applied stress multiplied by Poisson's ratio, which is about 0.3. If we take this value as one-third for purposes of easy discussion, it will be apparent that, in the case of the above referred to cube, similar prevention of plastic deformation occurs when two of the stresses are only one-third of the major stress, and as the value of these stresses varies above and below this amount, complex conditions arise whereby plastic deformation may be restrained without being completely prevented. It is important to realize that material in which plastic deformation is restrained is essentially and by definition brittle material and that by the above mechanism the softest iron may exhibit brittle failure.

With the above in mind the question of the welded structure may again be examined. Obviously, if the external stresses produced in this structure are at right angles to the applied stress and of sufficient magnitude, plastic deformation in the material is prevented and the material of the structure takes on the characteristics of brittle material. If the internal stresses at right angles to applied stress are of a lower order of magnitude, the same phenomenon results to a lesser degree. It should be noted that three-dimensional stresses are involved—not simply two dimensional.

Internal Stress at Right Angles to Plane of the Plate

The production of internal stresses parallel to the weld has been described, but no attempt has been made to ac-

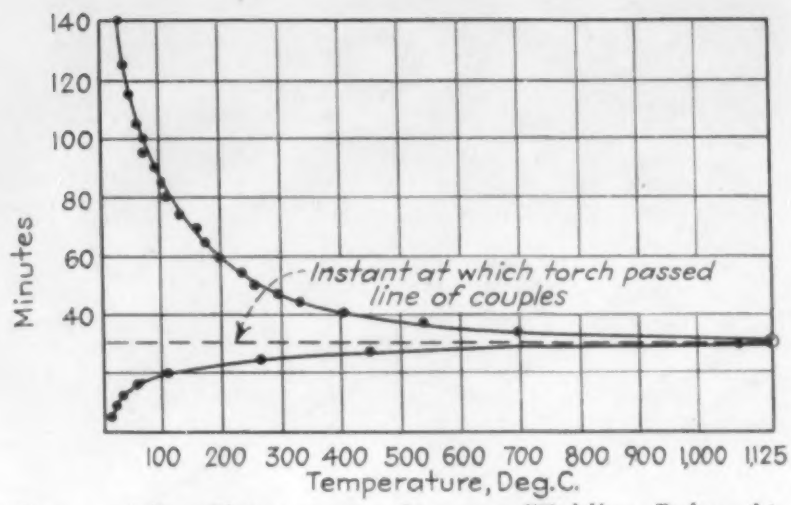


Fig. 4.—Time-Temperature Curve as Welding Point Approaches and Passes a Thermocouple Weld at Position 2, about 0.2 in. from Scarf of Weld.

count for internal stress at right angles to the plane of the plate. In fact the author knows of no wholly satisfactory explanation of the presence of this third dimensional stress. However, reasoning by analogy from the following experimental facts may afford some insight into this problem. If a hollow cylinder is subjected to axial tension, the diameter of this cylinder is reduced slightly up to the yield point, and then major reduction in diameter takes place as plastic deformation proceeds. If, however, the inside of the hollow cylinder is filled with a non-compressible material, the axial tension fails to produce any reduction in diameter of the cylinder as a whole. The non-compressible core reacts against the compressive forces to prevent motion, and the forces tending to produce motion as well as those tending to prevent motion may be considered as internal stress with reference to the structure as a whole. Thus, the restraint of motion at right angles to the applied force has resulted in internal stresses. This should be borne in mind in connection with the following argument.

If we now consider a thick plate in which internal stresses parallel to the surface of the plate are non-uniform, we can readily imagine any zone in the plate with low internal stress restraining motion of the adjacent zone carrying high internal stress, and by analogy with the aforementioned case of the cylinder this then becomes in effect the third

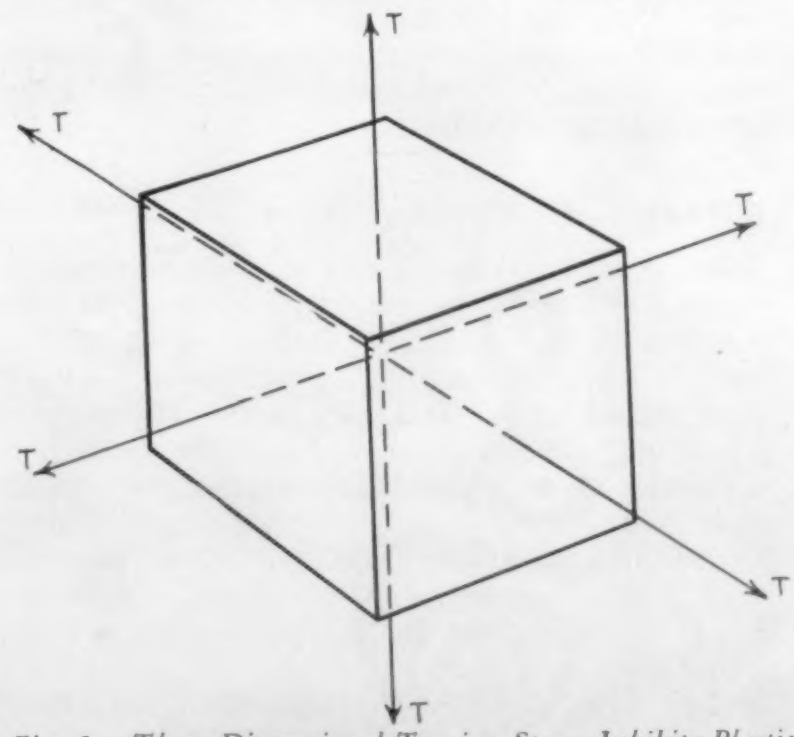


Fig. 5.—Three-Dimensional Tension Stress Inhibits Plastic Deformation.

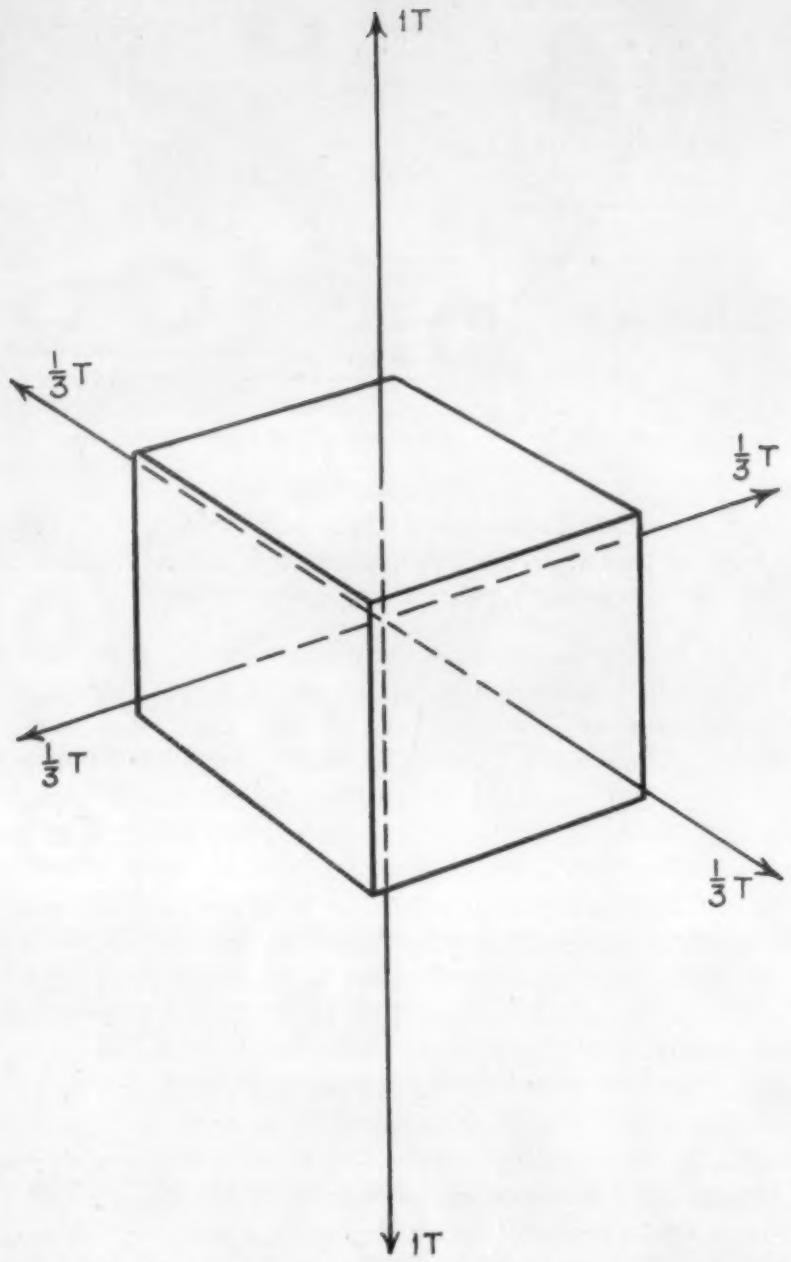


Fig. 6.—Three-Dimensional Tension Stress Inhibits Plastic Deformation.

dimensional stress at right angles to the plane of the plate. Again, the thinner the plate the less the chance for these internal stress gradients and the less restraint offered. In fact, at the surface there is no third dimensional restraint, and internal stresses at right angles to the surface can not exist. Thus, any difficulties due to the internal stresses should be very definitely minimized as the thickness of the material in question is reduced, and this conclusion is well substantiated by experience.

Effect of Thickness

The thickness of the welded material affects internal stresses in still another manner as these internal stresses may be effectively relieved by elastic deformation of the structure as a whole; for example, the buckling of a plate relieves internal stress. This brings us to the concept of flexural rigidity. It is obvious that a cylindrical tank 10 ft. in diameter with ¼-in. wall thickness has lower flexural rigidity and can deform elastically with consequent relief of internal stress to a very appreciable degree, whereas a "tank" 2 in. in diameter with ¼-in. wall thickness has high flexural rigidity and can distort elastically only to a very limited extent with practically no relief of internal stress. Similarly, a 2-in. diameter "tank" made of 20-gage material can deform elastically quite readily, whereas a 10-ft. tank with 4-in. wall thickness can not. Thus, while we frequently think of internal stresses in terms of the thickness of the material to be welded, it is generally necessary to modify our ideas and take the structure as a whole into consideration. Other things being equal, however, flexural rigidity will be greater the thicker the material in the structure, and the net result of this is again borne out by experience to the effect that thin-walled structures are not subject to dangerous internal stresses.

Summary

To summarize then, internal stresses are produced in unrestrained welded structures due to differential volume changes produced by temperature gradients, and the intensity of these internal stresses is largely determined by the steepness of the temperature gradient involved. Internal stresses parallel to the applied load are not to be considered of engineering consequence in such structures. Internal stresses at right angles to the applied load, if of sufficient magnitude, will effectively prevent plastic deformation. This condition, commonly known as "brittle," does not allow the material to accommodate itself to localized high stresses or suddenly applied stresses, and is most serious from an engineering standpoint. Such an internal stress condition is unlikely to occur in relatively thin-walled structures, but occurs with frequency and is a matter of serious engineering concern in heavy-walled structures. In such cases, stress relieving is essential. Any attempt to delimit thin-walled and thick-walled structures as used in the above sense must needs take into consideration not only the concept of flexural rigidity but also the magnitude of the internal stresses as a function of the thermal gradient which produces them, and this is a characteristic of the type of welding employed. The more intensely localized the welding heat the greater is the thermal gradient and the thinner the wall thickness, which would require stress relieving for conservative engineering practice. In the opinion of many, oxy-acetylene welded structures with free welds greater than 1 ft. in length and with plate thicker than ⅝ in. should be stress relieved, and structures welded with coated electrodes with free welds longer than 1 ft. and plate thickness greater than 5/16 in. should be stress relieved. This applies to structures in which there is no external restraint during the welding operation.

Stress relieving may be considered broadly as any means whereby the internal stresses are markedly reduced or eliminated. The commonly accepted method is to anneal the completed structure at approximately 1150 deg. F. Another method, which experience proves to be satisfactory when properly carried out, comprises peening of the weld. This produces a decrease in cross-section and increases the length and breadth of the member in question, thus effectively overcoming similar changes in the opposite sense, which occur in the welding operation. To generalize still further, any welded structure in which hardening of the base material occurs as a result of the welding operation should be stress relieved after welding, not only to eliminate the stresses but also to restore the material to a more ductile condition by the simultaneous tempering involved.

It is apparent that the problem of the nature and mechanism of production of internal stresses is not simple, that the effects of such internal stresses may or may not be serious, that such stresses may be readily eliminated, and that experience is sufficient so that the skilled welding engineer may judge if their elimination is economically warranted in any given case.

DIRECT ELECTRIC

Resistance Heating of Steel

FOR FORGING, UPSETTING, ETC.

by Fred P. Peters

Assistant Editor METALS AND ALLOYS.

ALTHOUGH HEATING STEEL for forming operations like forging and upsetting is entirely a preparatory function and not an end in itself, as is heating for annealing, normalizing, hardening, etc., the method of heating is a vital factor in the performance and economy of the whole operation and the quality of the finished part. The importance of the question impresses itself not only on the executive who may grow restive under high fuel or furnace costs, excessive scrap losses or customer's complaints about quality, but also on the hammerman that sees his dies wearing out too rapidly or not filling properly, and the furnace man that has to watch his stock "burn" because of overheating during hammer hold-ups. The heating of relatively small stock, from 1/4 to 4 in. diameter, and of uniform cross-section along the heated length is of most widespread interest, for it is from such stock that the large majority of production forgings are made. The question of method of heating also looms largest with the lower sizes of stock, as several methods are technically feasible for small stock and more than one in commercial use. With the heavier stock the operator's choice is definitely limited.

Practical Considerations of the Forging Operation

The selection of a method of heating small stock is influenced by several practical factors. Among the most important of these are *temperature* effects. The steel must be heated well above the critical range, so that it is in the austenitic condition and sufficiently plastic during working to fill the dies and assume the desired shape under the press or hammer. The precise temperature control required, for example, in heating high speed steel before quenching, is not necessary in heating forging stock, and, for the medium carbon unalloyed steel usually used, any temperature between 2000 and 2250 deg. F. is satisfactory. Forging is usually performed between 2250 and 1650 deg. F.

Although considerable latitude concerning temperature exists, there are definite limits. Temperatures above 2400 deg. F., for however short a time, should be avoided or "burning" (softening of the grain boundaries) will result and cause the steel to shatter under the hammer and ultimately to be scrapped. If "burnt" steel survives the forging operation it is brittle when cold and may fail in service. Holding the steel at temperatures less than 2400 deg. F. for too long a *time* induces pronounced grain growth and a consequently weak material. Grain growth, unlike "burning," is corrected to some extent by the grain-refining effect of the forging operation itself and may be further corrected by subsequent heat treatment. In general, the maximum safe temperature is lowered as the carbon content increases.[1]

If the forging temperature of the steel is too low, or as occasionally happens, if the stock is hot enough outside but has a cold, hard core, internal strains or cracks and erratic filling of the dies will result. The hammerman also wants his stock to come to him at approximately the same temperature each time so that successive forgings will fill the dies in a uniform fashion.

The *rate of heating* is of great importance if the heat is applied externally as in the conventional furnace, for the rate at which the heat is transmitted within the stock is fixed by its conductivity and diffusivity. Too rapid heating from the outside causes differential thermal expansion and therefore severe dimensional changes as the steel passes through the critical range, and causes it to crack or "clink."

With small stock, the metal lost through *scaling* is of negligible importance but excessive scaling greatly reduces die life and results in a poor surface if an adherent scale is forged into the part. For these reasons scaling is an important factor. Slow heating tends towards excessive scaling if the stock is heated in air or in the products of complete combustion.

Ideal Requirements of Forge-Heating Equipment

From these practical considerations, the requirements of ideal equipment for heating steel for forging may be outlined.

First, for the most economical production, the stock should be fed to the hammer or press as fast as the latter can take it, as idle forging equipment usually represents a tremendous loss in overhead charges. Most heating equipment is therefore designed to err on the hot side, possesses excess thermal capacity and accordingly responds slowly to shutting-off when danger of overheating is imminent.

In practical opposition to this is the desirability of having heating equipment that cannot overheat the metal, particularly during hammer hold-ups. The serious impairment of

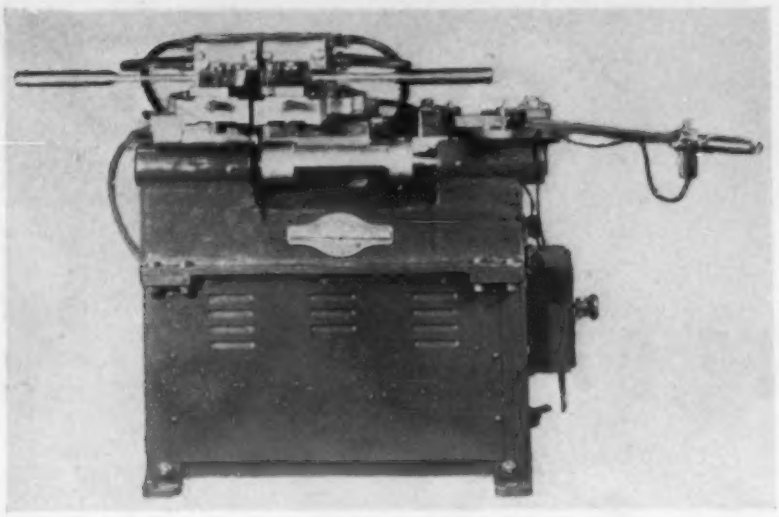


Fig. 1.—Butt Welder that Can Be Adapted to Resistance Heating of Steel for Forging. (Courtesy Thomson-Gibb Electric Co., Lynn, Mass.)

quality resulting from "burning" or overheating has already been discussed.

The method of heating should be such as to avoid the differential thermal expansion and consequent clinking associated with too rapid application of heat from the outside.

Stock should be delivered to the hammerman with successive pieces at approximately the same temperature. Also the distribution of heat should be uniform throughout the cross-section of each piece, a condition that must usually be achieved by "soaking" at temperature for sufficient time.

The method of heating should result in a minimum of scaling, to avoid excessive die wear and poor surface.

The cost of the heating process, including amortized cost of the equipment itself, cost of the heating energy and labor charges should be satisfactory.

Available Heating Methods

There are 5 generally available methods of heating small stock for forging: gas-fired furnaces, oil-fired furnaces, electric furnaces, induction heating and direct resistance heating. The first 3 may be classed together as *indirect* heating methods, for in them the heat is transmitted to the stock by radiation from the source; the last 2 can be grouped together as *direct* heating processes, for the heat in both cases is developed in the stock by the passage of electric current through it.

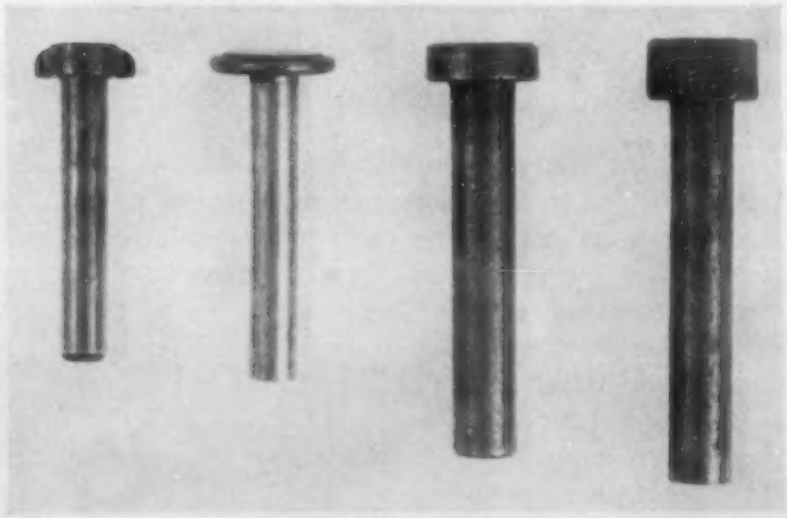
By far the majority of production forgings are heated by indirect methods, chiefly gas or oil-fired furnaces. More general use of the electric furnace has been limited by the relatively short life and therefore high cost of the resistors available in the past. For most operating programs the gas and oil-fired furnaces are entirely satisfactory, particularly where furnace and hammer have been well synchronized and workers are careful to control the temperature, time and rate of heating to avoid the difficulties previously described. Not always, however, is close operating control achieved, and in such cases gas or oil-fired furnaces depart considerably from the ideal heating method. Thus, although indirect methods invariably succeed in keeping ahead of the forging equipment, they do offer the possibility of over-heating or "burning" the metal in the process, as the customary excess thermal capacity prevents rapid reduction of temperature during hammer delays. And not infrequently the stock suffers when the too rapid rate of heating piles the heat at the surface of the stock and causes "clinking", or, if the stock be removed to the forge too quickly, results in a satisfactorily plastic surface but a cold, hard core. If the rate of heating be reduced, the likelihood of excessive scaling becomes a problem. The question of economy varies from job to job; in many cases, particularly as the size of stock increases, the indirect methods can show an operating cost advantage.

The major problem in the use of the conventional forging furnace involves balancing these opposing factors. As Jominy[2] has pointed out, "quite commonly sufficient room is not available in the forge shop for furnaces of such size that slow heating to a proper forging temperature is possible. The result is undersized, overheated furnaces in which the steel cannot be permitted to reach the furnace temperature if burning is to be avoided. Such furnaces are usually the slot type in which the back of the furnace is much hotter than the front. Using this type of furnace we are entirely dependent upon the man in charge of heating the steel for safe forgings." Direct methods of heating are considerably more fool-proof.

The use of high-frequency induction for the heating of steel for forging has recently been described.[3] This method shares with the direct resistance method the advantages of quick heating developed within the stock itself (although with induction heating the surface is initially hotter than the center), minimum of scaling and certainty of control, and is superior to the latter in that contact difficulties are absent. Although the cost of the generating equipment is prohibitive for many jobs, the use of induction heating for this purpose will probably be extended as time goes on.

The apparent advantages inherent in the use of the fifth (direct resistance) method of heating are so great that the following extended examination of its present applications, the types of equipment available and user's experience with the method appears warranted.

Fig. 2.—Samples of Products of the Combination Electric Heating and Forging Machine. (Courtesy National Machinery Co., Tiffin, Ohio.)



Direct Resistance Heating

In the direct electric resistance method of heating steel, an electric current at relatively low voltage is passed through the metal, which becomes itself a "resistor" and assumes some temperature depending, for a material of given composition, cross-section and length, on the electrical energy applied. The mathematical relations between the many factors that determine the final temperature of a piece of resistance-heated steel, the time required to reach it and the power consumed in the process have been given by Knill.[4]

For a given material at constant voltage, the temperature is higher the lower the electrical resistance and the smaller the radiating surface of the heated piece. The resistance, in turn, decreases with increasing cross-sectional area and decreasing length. The time required and power consumption for reaching a given temperature at given voltage increase with the heat content of the piece at the temperature, or in other words with its specific heat and mass, and increase in proportion to the energy lost through thermal radiation, convection and conduction.

Because resistance heating is "heating from within" the piece, the center of a heated bar is hotter than its surface, which is losing heat to the surroundings by radiation and convection, and than its ends, which are losing heat by conduction through the grips or electrical contacts. For practical purposes, however, the cross-section gradient is negligible, and during the heating-up period the temperature increases simultaneously and uniformly throughout the section; dimensional changes, and therefore cracking or "clinking," caused by differential thermal expansion are absent. From the "quality" standpoint this is an important advantage possessed by the direct resistance method over other heating methods, where heat is applied to the piece indirectly from the outside.

The internal generation of heat also avoids the serious danger of obtaining a sufficiently hot surface, but a cold, hard core, as the center is always at least as hot as the outside. The importance of this is obvious in view of the usual practice of estimating temperature by observation of the *surface* of the stock.

Again, because of the direct generation of heat within the stock, heating is much more rapid than that obtained by the indirect methods. Because of the cross-sectional thermal uniformity just mentioned, this high rate of heating may be fully utilized to supply material to the hammer or press more rapidly than might be possible otherwise. It is necessary to point out here, however, that although a single bar is heated more rapidly by the resistance than by conventional furnace methods, the latter may consume less time in the aggregate because of their greater capacity, as many bars may be heated in a furnace simultaneously, if necessary, to meet a particular forging schedule. When furnace control and synchronization with the hammer are perfect, the resistance method would probably offer little, if any, direct time advantage; in all cases, however, it does provide rapid heating without the slightest danger of quality impairment.

An unquestioned advantage inherent in the short heating-up time is the relatively small amount of scale produced. As previously noted, heavy scaling shortens die life and may detract from the surface quality of the forged part. With small stock, scaling during resistance heating is negligible and, because of the usually greater importance of surface quality in the smaller sizes (1/4-1 in.) resistance heating is frequently selected solely because of the reduced scaling factor. Although with heavier sizes surface quality may not be paramount, the metal loss through scaling becomes a consideration, and here, too, resistance heating may offer some saving.

"Burning" and overheating (grain growth) may be completely avoided, because of the close, individual control of temperature and time that is possible. The majority of resistance heaters include photocell control, so that current is shut off as soon as the piece reaches a predetermined temperature. Thus, not only is overheating prevented but uniformity of temperature from piece to piece is guaranteed.

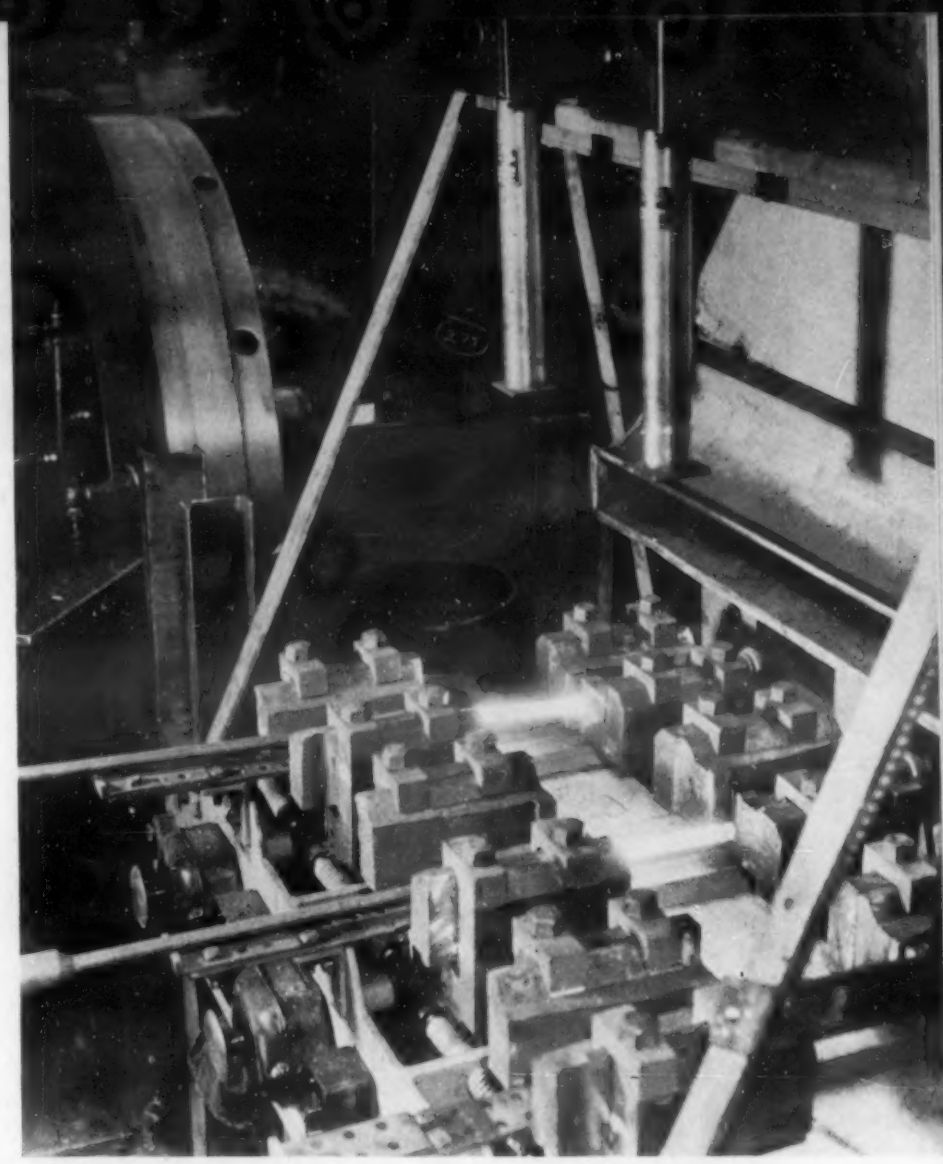


Fig. 3.—ACF Manual-Feed Berwick Electric Forging Heater in Operation at an Automotive Plant. (Courtesy Chevrolet Motors Corporation, Bay City, Mich.)

Where photocell control is not provided, the voltage can be set to avoid *burning*, but *grain-growth* may occur through holding at temperature for too long a time if the operation is not watched.

In some cases direct resistance heating has definite disadvantages as compared to conventional furnace methods. To date the maximum size of stock capable of being heated in this fashion is 2 1/2 in. diameter; furthermore the length to be heated must be of uniform cross-section throughout if temperature uniformity along the length is desired, for the resistance of the piece and therefore its temperature at any point are a function of its thickness. Also, the heat loss by conduction through the grips or contacts at the ends of the heated length may be sufficient to prevent the ends from reaching the temperature of the rest of the bar. Some trouble with pitting at the contacts has also been reported, although this objection does not seem to be generally serious.

General Applications

Before discussing equipment available for resistance heating of forgings, upsets, etc., some mention of other metallurgical applications of this method should be made. Trautman[5] describes the heat treatment of spring wire by an electric resistance method, in which wire is fed from reels through tension rolls, with individually controlled contact members. Wire temperature is controlled automatically by photocell, in conjunction with voltage regulators, giving temperature fluctuation no greater than 5 deg. F. Among the advantages cited are greater uniformity through the cross-section, absence of decarburization and scaling, high thermal efficiency (95 per cent), ease of control, and the

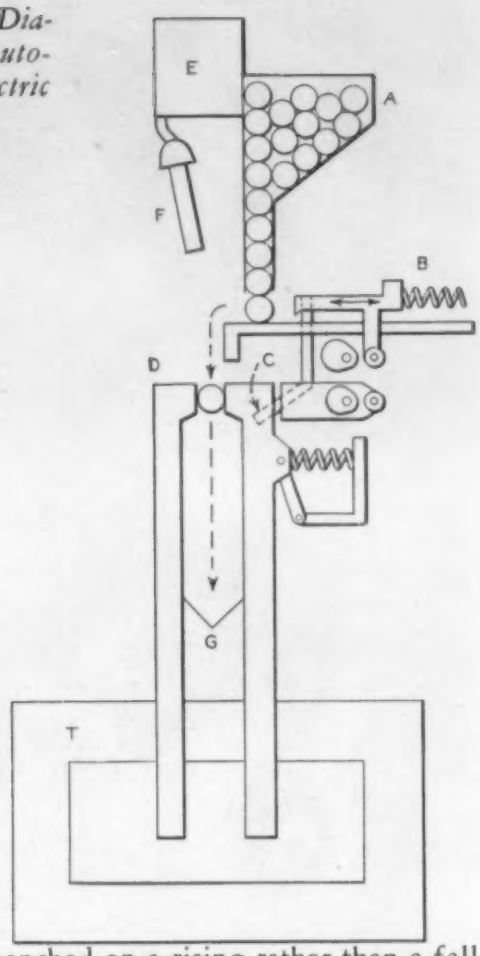


Fig. 4.—Operating Diagram of ACF Fully-Automatic Berwick Electric Forging Heater.

fact that the wire is quenched on a rising rather than a falling temperature.

The Snead process[6] was an early attempt to apply the direct resistance method to the heat treatment of steel. In this process long bars of uniform cross section were gripped at the ends by large clamps, through which the current was passed; the extension of the stock due to thermal expansion actuated relays which indicated and controlled the temperature of the steel. Because the stock failed to reach the proper temperature in the neighborhood of the heavy clamps, the distance between the latter was usually made greater than the length required to be heated.

Wylie[7] has recently given a detailed description of somewhat similar apparatus and practice for the direct resistance heating of long aircraft members for hardening or tempering. The process is called the "Tension Electric Process" and is stated to be employed with great success by Armstrong Whitworth Aircraft, Ltd., of England. Air hardening steel bars up to 30 ft. long and 1 sq. in. cross-sectional area are end-held by metal grips, and without other support are heated rapidly to a uniform temperature, held there for a few seconds, and then allowed to cool in air. The appreciable changes in length that occur with such long members are accommodated by making one of the grips movable; tension is then applied to it during the treatment. Current is fed to the bar through the fixed grip and the movable carriage at the opposite end, and temperatures are measured with an optical pyrometer. The process is "absolutely guaranteed to give uniformly correct temperatures"; it is assumed the sponsor qualifies this in practice to allow for variation in thickness along the bar, for with such long stock, absolute uniformity of cross-section must be something less than fact. Also, because of heat loss by conduction, the correct hardness is admittedly not attained in the neighborhood of the grips. Although no cost figures are given, the installation and operating economy of the Tension Electric Process are claimed to be excellent for the output obtained. The process is of considerable interest because of the very great length of stock handled, but, also for the same reason, its possible economy is difficult to perceive.

The hardening of high speed steel hack saw blades by direct resistance heating has been described by Trickett.[8] The blades are held in tension with heavy contact-clamps, current is passed, and, as in the Snead process, the thermal expansion of the steel acts as a temperature indicator. The blade is hardened by air cooling; in this case the failure of the steel to reach hardening temperature around the clamps is a real advantage, for the ends of the blade thus remain soft, and subsequent annealing of them is obviated. This feature also permits the use of larger clamps than can ordinarily be used in resistance heating.

The adaptation of welding equipment to the heating of steel for annealing or upsetting is an interesting application of direct resistance heating. For example, the design of a simple fixture, which when fitted to a 10 kva. spot welder permits use of the latter for annealing a restricted area of an automotive stamping prior to forming has been given in a recent note in *Steel*.[9] The shanks are attached to the upper and lower arms of the welder and current is directed as desired by adjusting an arrangement of contacts and insulating blocks. The Thomson-Gibb Electric Welding Co. also reports the use of butt welders for upset welding the collar midway along the length of a valve stem,[10] and for upsetting integral collars in the middle or on the end of valve stems.[11] In the former, two pieces of stock slightly larger than finished size are simply placed in the electrodes and forced together until the joint bulges enough to produce a lump from which the collar can be machined. The equipment is also applied to the more common process of producing upsets from single lengths of stock by the use of clamps or blocks at the electrodes. The heads of poppet valves can be built up on valve stems by using a solid block instead of one of the electrode clamps, and the work can be done in a machine that automatically feeds the stock and cuts off and ejects enough material for each valve. In one automobile plant a batch of several thousand forgings (a yoke-shaped clutch release) apparently spoiled because a forging die had not been properly designed was salvaged by clamping the forgings in a butt welder, heating to 1500 deg. and bending to the exact angle required. The equipment used for this is illustrated in Fig. 1.

The combination heater and forging machine manufactured by the National Machinery Co. finds particular application for the continuous, automatic hot-heading of bolts.[12] The wire is fed directly from a coil, the blank is cut off and, during transfer from the cut-off stage to the heading stage in a revolving drum, is heated by a 3-stage electric resistance heater, then headed and ejected. This machine is particularly useful for the production of parts with scale-free shanks from material that cannot be successfully cold-headed; typical products of this equipment are shown in Fig. 2. Because of the close temperature control possible, this combination heating and forging machine is also being used for handling parts forged from brass stock.

The Berwick Rivet Heaters

Probably the pioneer in the field of electric resistance heating was the Berwick Electric Rivet Heater, introduced by the American Car and Foundry Co. in 1913. The first heaters[13] consisted of a transformer with a low-voltage, high-current single turn secondary winding placed directly

over the primary. The rivet was inserted in the secondary circuit and held in place by spring pressure on the electrodes. The rivet heaters have since been steadily improved, chiefly in their electrical design, and have found a wide market because of the rapid, clean and "comfortable" production obtained with them.

With the rivet heaters the cost of operating power is a large proportion of the unit cost for the equipment and hence must be considered if selection of heating method is to be based on economy alone. Where electric rates are low the electric rivet heaters can show a much lower operating cost than heating by gas or oil; with high power rates, however, or where the demand schedule is unfavorable, their operating economy may not be so marked. The American Car & Foundry Co. in its Buffalo plant reported a heating cost of \$0.16¼ per 100 lbs. of rivets. In another car plant (not affiliated with the heater manufacturer), a comparison between oil heating and resistance heating showed a heating cost per 100 lbs. of rivets of \$0.454 with oil and \$0.104 with resistance heating. In the former case current cost was \$0.0086 per kw.-hr., in the second \$0.0055 per kw.-hr. The latter figure is about the lowest power cost one can expect in this country and in some plants the cost of electricity may be three or four times this minimum. A very rough estimate of the heating cost for a given job may be made, however, as 100 lbs. of rivets require 11 to 20 kw.-hr. for satisfactory heating, depending on the length and diameter of the rivets. Impartial operating tests on the rivet heaters have shown that their power consumption is frequently as low as 33% of the theoretical values given by the American Car and Foundry Co. in their literature.

Berwick Forging Heaters

The field of application of the early Berwick heaters was extended to cover other metallurgical uses than rivet heating, so that now several types of large and small resistance heaters are available for heating, for forging and upsetting, stock from ¼ to 2½ in. thick and up to 6 ft. long. Some particular applications of and users' experiences with the Berwick electric metal heaters will be described later.

The operation of the Berwick heater is quite simple. The larger heaters for handling heavy stock are manually fed; small heaters with mechanical feed and fully automatic operation are available for light stock. All heaters are equipped with photoelectric controllers over the electrodes that may be set to cut off the current when the desired temperature is reached, and which therefore prevent over or under-heating of the stock.

With the manually-fed heaters the stock is inserted in the electrodes; a push-button closes the electrodes on the cold piece; current passes until the desired temperature is reached, when the photocell and controller operate to open the electrode jaws. The operator then removes the heated stock, and inserts the next cold bar and pushes the button to renew the cycle. All electrodes have movable blocks with contact points for length adjustment; a cam-shaft controls the opening of the electrodes, and, with a given heater, no adjustment is necessary for different diameters. Fig. 3 shows a manual-feed Berwick heater in operation at Chevrolet's Bay City plant.

The operation of the fully automatic heaters, capable of handling stock from ¼ to 1¼ in. in diameter and up to 2 ft. long, is illustrated in Fig. 4. Stock is placed in the

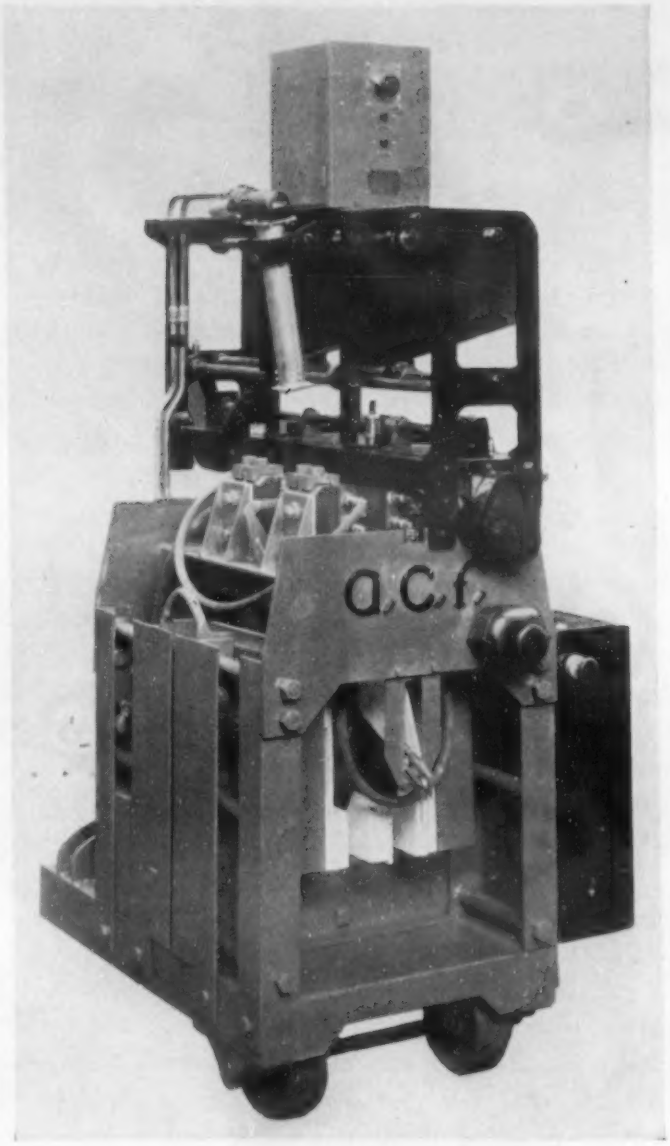


Fig. 5.—Front View of latest Model ACF Fully-Automatic Berwick Electric Forging Heater.

hopper A, where it settles into the vertical spout; the pieces are agitated by cams on the revolving shaft to avoid clogging. As the electrodes open, the material pusher B moves and pushes the lowest bar in the column over the ledge on to the rest C which has moved to the left with B. The electrodes D (the right electrode is movable) then close and with a simultaneous motion B and C return to their original positions. When the piece reaches the proper temperature the electric eye and controller cut off the current from the transformer T, open the electrodes and the piece drops down to the inclined roller chute, G, which deposits it, cold end up, into a receiving cup placed near the forging or upsetting machine. As the electrodes open, the pusher B pushes the next piece over the ledge and the cycle is repeated. The heaters are provided with a "kicker" to eject the heated piece in the event of fusing or sticking to the electrodes. In the earlier heaters this kicker was solenoid-actuated, but the present mechanical kicker has been found much more satisfactory. Also, in the latest models (See Fig. 5) the electrode jaws are water-cooled to reduce deterioration of the contacts, and the lead-wires to the photocell are carried in four conduits, rather than one, to eliminate the effect of surges in one circuit on the sensitive relays in the others.

The manual-feed heaters are furnished with one, two or three electrodes, and the automatic with either one or two, with an equal number of photocells and controllers in any case. Vedder and Evans[13] have given a good description of the electrical circuits and particularly of the photoelectric equipment and its operation. Limit switches are

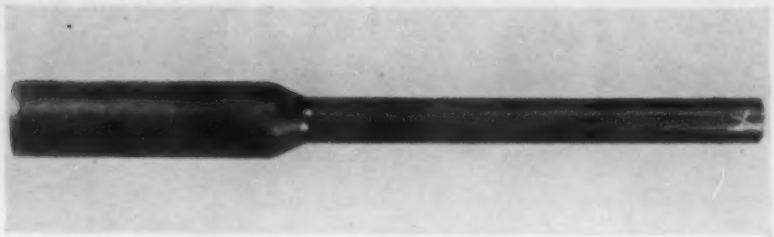


Fig. 6.—Drag Link Forging Produced by Saginaw Steering Gear Division of General Motors Corp., Saginaw, Mich. Stock is heated in Berwick Heater and forged in National Machinery Co. equipment. (Courtesy National Machinery Co., Tiffin, Ohio.)

used to actuate the main contactor and prevent power going to the transformer until the grips are perfect; the importance of this in reducing surface pitting of the stock at the contacts is evident. According to them only by the use of the photocell can current shut-off at the transformer primary be made simultaneously with attainment of correct temperature. Without such close control resistance heating could not be practical, from the metallurgical viewpoint. Methods based on the thermal expansion of the stock or on the use of bimetallic thermo-elements are not sufficiently sensitive.

Users' Experiences with Resistance Heaters

The advantages claimed for the Berwick heater by its sponsors are about the same as those mentioned earlier in this article as characteristic of the general process of resistance heating. The actual existence of most of these is undeniable, but adoption of this method in any case depends on the extent to which these obvious advantages are counterbalanced by other factors. Inasmuch as the most accurate appraisal of the merits of any product or process lies in users' experience therewith, a few typical applications of the Berwick heater will be described.

At a Chicago Plant

One of the earliest installations of the two-electrode fully automatic heaters, at a Chicago plant, was used for heating the end of bolt stock before bending it into a simple right-angle head. This heater (ACF No. 3) handles stock between 1/4 and 1 in. thick, and at the plant in question several sizes within this range are heated; some interesting observations on the relation of size of stock to the usefulness of a particular heater resulted. The first installation was recently replaced with 2 single-electrode fully automatic heaters, and the author had an opportunity to observe one of these in action at the plant:

An 0.20 per cent C stock, of 5/8 in. diam. was heated to 1800 deg. F. along 3 1/2 in. at one end (the minimum length of end heat possible with this type of heater is 1 3/8 in.), discharged automatically into a container and the right-angle end-bend made immediately in a small machine. The stock, before being placed in the hopper, was pickled and degreased in an alkaline cleaner, and, after the forging operation, was lightly pickled. Actual timing of the heating cycle showed that the total cycle required 11 sec. (production was 5.5 pieces per min.) and each piece was at temperature about 7 sec. Scaling was very slight and pitting at the contacts was not evident, probably because of the previously clean surface of the stock.

Queried as to the merits of the equipment, the superintendent replied that he liked it chiefly because of its convenience and fool-proof nature, although he questioned its economy. The unit can be started up cold without having to wait several hours before stock can be charged, is very comfortable for the operators, and, owing to its automatic nature, probably saves something on labor. The total production on this job, however, and particularly with this size stock, is less than with batch type oil-fired forging furnaces. This was apparent from watching the operation —a good workman could handle this simple forging operation faster than stock was supplied to him by the heater. On lighter stock than this, heating is of course more rapid, and in such cases the superintendent believes the Berwick heater has a time advantage over conventional furnaces. In short, this company's experience is that the convenience, cleanliness and attendant quality of the Berwick heater make it an attractive proposition where rigorous economy is unnecessary.

At a Massachusetts Plant

The use of the manually operated heaters, handling much heavier stock, is well illustrated by the installation at the Massachusetts plant of a large manufacturer of textile machinery. This company has used the resistance method of heating bar stock before forging into loom crankshafts for over 6 yrs., and at present has three manually operated 3-electrode heaters. The stock is forged in various thicknesses between 1 1/2 and 2 1/4 in.; the latter size represents the largest diameter for which the Berwick heaters are in commercial application anywhere. The author recently visited this plant, observed the heating and forging operation and discussed the method with its staff:

The stock used is S. A. E. X-1335 (0.30-0.40 per cent C, 1.35-1.65 Mn, 0.075-0.15 S) and is evidently standard for such crankshafts in the industry. The forging temperature is 1950 deg. F. and the forging itself is a three-stage operation using two machines. The 1 1/2 in. stock is heated for about 2 ft. between points somewhat removed from the end of the piece and the total heating cycle for each piece is 4 min. There is no conscious "soaking" of the stock at temperature, although the operators stated that a heating-up time of 2 min. is sufficient. During our visit two heaters, or six units, were in operation; one man ran the heaters, two others the forging machines. The total production of both heaters averaged about 6 pieces every 12 min. or 2 min. per piece, just fast enough to keep all three men moving at a lively pace.

At the Chicago installation previously described, using relatively light stock, there was a size of stock below which the Berwick heater was time-saving and above which it was not. At the Massachusetts plant, however, there is considerable excess capacity in the equipment. With all six units in use on 1 1/2-in. stock, and the heater operator feeding a new bar somewhere every 2 min., the heater tended to run ahead of the forge operators, so that not all six are actually required; with 2 to 2 1/4-in. stock all units are required and the heater and forge operators keep approximately in step with each other.

The stock is previously ground off at the contact points to avoid pitting and excessive heating at the electrodes. Pitting would not seem to be detrimental here, for in any case the surface in the neighborhood of at least one of the contacts must be smooth-machined later. During heating the stock scales very little even with (for this type of heating) the relatively long time at higher temperatures. Except for the aforementioned machining, there is no subsequent pickle or descaling operation.

The rated voltage of the equipment we observed was 550 volts. At the beginning of heating, with three 1 1/2-in. bars in the line, the heater drew 250 amps; with one

2¼-in. bar (heating time 5 min.) being heated, 105 amps. were consumed. Current demand of course, drops as the piece heats up, owing to the effect of temperature on electrical resistance.

Operating tests on an earlier heater installation at this same plant have been made by the utility serving it and are given in the Table as an indication of the electrical performance of the equipment. The performance of later heaters has been considerably improved, so that these figures must be considered as the worst that can be expected of the Berwick heater.

Table of Summary of Test Results on an Early 3-Electrode Manual-Feed Berwick Heater.

Item	1½ in. bar.	1¾ in. bar
Average production over entire run	2.1 min./piece	3.17
Average power consumption over entire run	2.45 kw.-hr./piece	3.7
Actual time to heat one rod (average)	5.47 min.	6.35
Max. instantaneous demand	160 kw.	175
Max. 15 min. demand	71.5 kw.	77.3
Average load during test run	70 kw.	70
No. pieces heated	47	12
Total time required	1 hr., 39 min.	38 min.
Total energy consumed	115.1 kw.-hr.	44.4
Unit cost of energy for 200 pieces per day	$0.01575/kw.-hr.	
Unit cost of energy for 150 pieces per day		$0.01505.kw.-hr.
Cost per piece	$0.0386	$0.0567
Capacity of heater	250 pieces/9hrs.	150

This company had found the Berwick heater to have the following advantages for its application: (1) The negligible scaling of the stock. (2) The confinement of the heat practically to the length to be forged. The ends of the bar (which is about 6 ft. long) need not be heated, (3) Comfort to the workmen—this was apparent as there were some oil-fired furnaces in the room that made an inferno of their neighborhood, while the temperature close to the Berwick heaters was quite comfortable. (4) An "apparent" saving in fuel consumption; no comparative figures were available. (5) Ease and accuracy of temperature control, uniformity of treatment and low shrinkage. (6) Immediate availability of service at any time.

The disadvantages cited were: (1) Apparent wear of the electrode parts, causing occasional failure of the grips to come together properly, and certain other mechanical difficulties. (2) Impossibility of using a preheated piece where the stock is not at the same temperature in the neighborhood of the contact points. (3) Uselessness of the Berwick heater for stock of tapering or otherwise non-uniform cross-section.

For this company, the advantages far outweigh the disadvantages, as it is gradually replacing its oil-fired furnaces for similar jobs with Berwick heaters.

At a General Motors Plant

A third interesting application of the resistance heaters is at the plant of the Saginaw Steering Gear Division of General Motors Corp., Saginaw, Mich., where they are used for heating ¾-in. stock before upsetting and forming automotive drag links. The finished forging is shown in Fig. 6. This company has 3 Berwick heaters, each a manually operated 3-electrode machine, equipped, as are all the heaters, with photoelectric control for each electrode.

The material used is ¾-in. hot-rolled 0.20 C steel, which is previously tumbled to remove the hot-mill scale that would otherwise cause improper contact and, therefore, pitting at the electrodes. The heats are end-heats, either 4 in. or 6½ in. depending on the length of stock to be forged. When the end of the bar is heated to 2100 deg. F. the photoelectric controller opens the electrode jaws, which stay open for a short time and then close again and resume heating if the bar has not been removed; this opening and closing continues until the operator removes the stock. The time required to heat the 4 in. length is 21 sec., and to heat the 6½ in. length, 24 sec. The number of pieces produced per hour, however, is controlled in this case by the speed of the forging operation, which is slower than the maximum possible production rate of the heater. Thus, using only two out of three sets of electrodes, the operators produce 110 long ends and 140 short ends per hour. The machine is capable of heating 50 per cent more work per hour if the forging operation were faster.

The scale formed is of paper thinness and need not be removed in subsequent operations. This company is not bothered by pitting at the point of contact, and believes that such surface marring can be eliminated by care and maintenance of the electrode blocks. Extra sets of blocks with flat-milled contact surfaces are kept on hand and the contacts changed once every day.

On the basis of a required energy input of 16.3 kw.-hr. per 100 lbs. of steel heated, Saginaw estimates the heating cost to be $0.178 per 100 parts heated by the electric resistance method and $0.134 for the same number of parts heated in a gas furnace, the method formerly used. The cost of electricity in this case is $0.011 per kw.-hr.

This company summarizes its experience as follows: The use of the Berwick heaters is not so economical, at least with respect to the "fuel" cost, as the use of gas or oil-fired furnaces. This increase in operating cost, however, is more than offset by the convenience, the excellent surface quality and the more positive temperature control available in the resistance heating method.

Conclusion

The combined experience of these and other users indicates that the direct electric resistance method of heating steel merits, on the basis of quality alone, much wider consideration. The present operating economy of the resistance heaters is questionable; for some jobs there is evidence that the resistance method is more economical, while for others there appears conclusive proof that other methods are less costly. However, the heaters have been greatly improved in recent years; there is good reason to believe that the operating cost may be further reduced and that some of the annoying contact difficulties still experienced may be eliminated in time. And, whatever its present relative operating cost, the direct resistance method is unquestionably the most convenient and fool-proof available today.

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Courtesy: H. W. Fortey, Warner & Swasey, Cleveland

Cutting Gear Blanks on a W. & S. No. 5 Turret Lathe

THE MICROSTRUCTURES OF

MO-MAX AND 18-4-1

HIGH SPEED STEELS COMPARED

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THE SET OF MICROGRAPHS accompanying this brief discussion, was originally prepared for the use of steel mill metallurgists who were studying the heat treatment of "Mo-Max" molybdenum-tungsten high speed steel. It met with such a favorable reception that it is now thought that others may also be interested. It illustrates the structures of these two standard types of high speed steels after a variety of heat treatments. Every effort has been made to keep all conditions which might affect the microstructures strictly comparable. The conclusion has been reached that with comparable heat treatments it is not possible to distinguish between the structures of these two types of high speed steel.

The analyses of the steels used are as follows:

	Mo-Max	18-4-1
Carbon	0.80	0.70
Manganese	0.16	0.34
Silicon	0.29	0.36
Chromium	3.65	3.90
Tungsten	1.35	18.00
Molybdenum	9.01	none
Vanadium	1.23	1.04

The specimen size was 5/16 in. diameter by 1 in. long. In comparing these microstructures with those of tools of a size greatly different from this, the possible effects due to the mass of the tool should be considered.

All specimens were hardened in a salt bath. No preheating was used. Hardening times, except when otherwise noted, consisted of 30 secs. soak at the hardening temperature preceded by a period of about one to two minutes required for the specimen to reach the temperature of the salt bath. All specimens were quenched from the hardening temperature into oil at a temperature of about 80 deg. F.

Tempering was done in a lead bath. Tempering times consisted of 30 mins. soak at the tempering temperature, preceded by periods of 5 to 10 mins. required for specimens to reach the temperature of the lead tempering bath. The specimens were cooled from the tempering temperature in still air.

Flats were carefully ground on each specimen parallel to the cylindrical axis (direction of rolling) and then the specimens were polished. Each specimen was etched immediately after polishing so that no oxide film could form. In this way, comparable etching times were obtained. An etching period of 2½ mins. in 6 per cent nital was used for all specimens so that any differences in the tone of the matrix could be attributed to actual structural differences in the specimens. The micrographs were printed in a manner to make them resemble as nearly as possible their appearance when observed through the eyepiece of the microscope.

In the following discussion of the microstructures, it should be pointed out that the structures which are called *normal* represent hardening temperatures usually used for drills, reamers, milling cutters and similar tools, but not necessarily for lathe tools. Where great red-hardness is the principal requirement, as in lathe tools used for heavy roughing cuts, higher hardening temperatures than those producing the normal structures would be used.

Normal Structure—Figs. 1 and 2

Both Mo-Max and 18-4-1 show well defined austenitic grain boundaries, the grains in both steels being of moderate size (about 0.0006 in. in diameter on the specimen or 1.2 in. on the micrographs).

The martensitic needles are definitely outlined by dark troostite for both steels and are slightly acicular in shape, being slightly more needle-like in the Mo-Max than in the 18-4-1. The higher Rockwell hardness of the Mo-Max can be directly attributed to the higher carbon content of its martensitic matrix.

The carbides are numerous and well distributed in both steels. They are slightly rounded with a few slightly angular in shape.

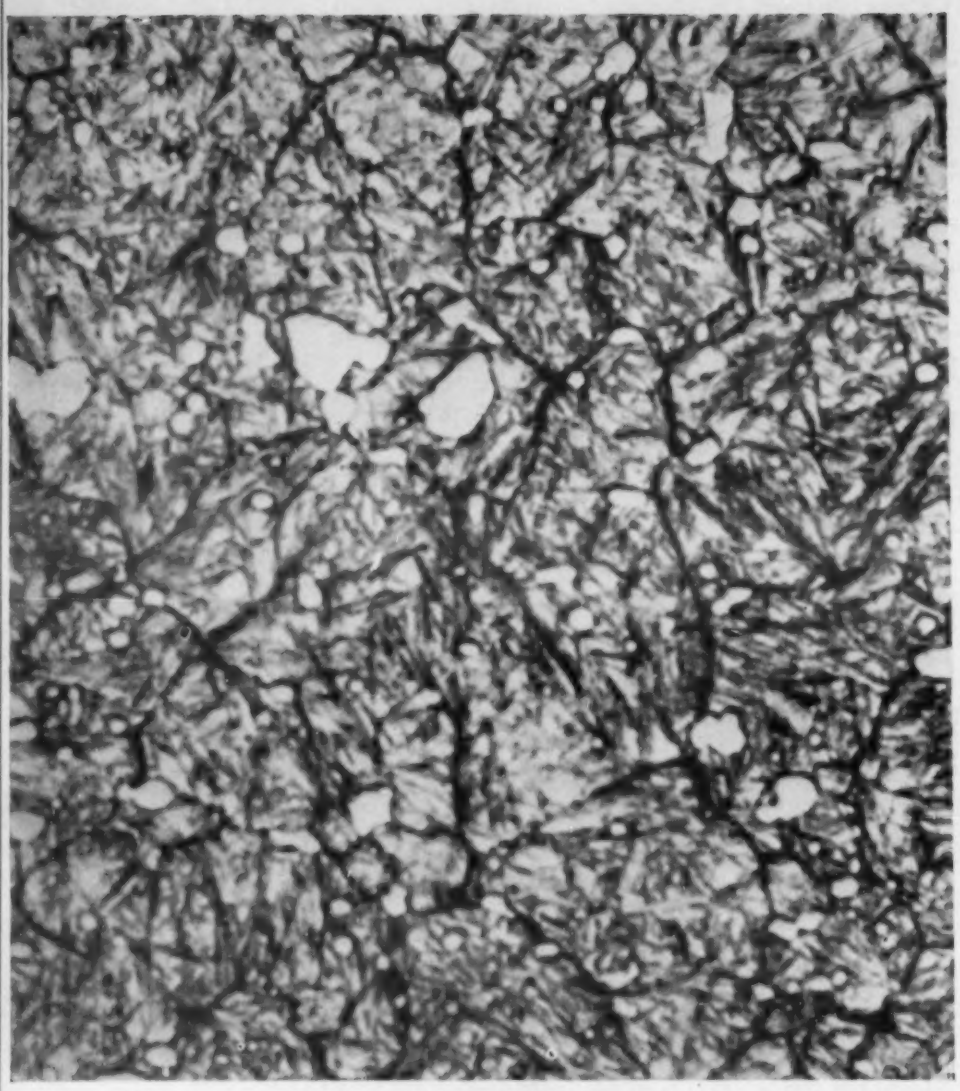


Fig. 1.—Mo-Max, Normal Structure. X 2000. Etched for 2½ mins. in 6% nital. Hardened at 2220 deg. F. for 30 secs. Tempered at 1040 deg. F. for 30 mins. Rockwell C—66.9

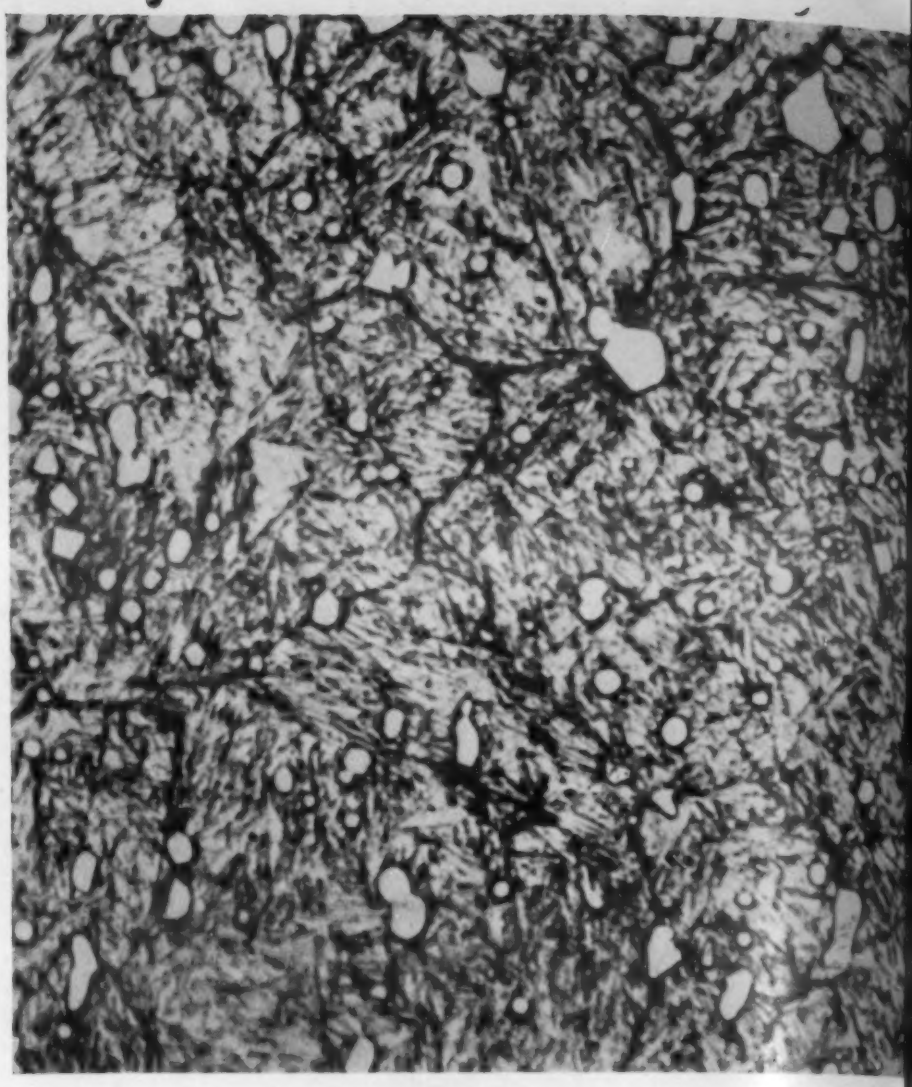


Fig. 2.—High Speed, Normal Structure. X 2000. Etched for 2½ min in 6% nital. Hardened at 2380 deg. F. for 30 secs. Tempered at 104 deg.F. for 30 mins. Rockwell C—65.7

Fig. 3.—Mo-Max, Slightly Underhardened. X 2000. Etched for 2½ mins. in 6% nital. Hardened at 2150 deg. F. for 30 secs. Tempered at 1040 deg. F. for 30 mins. Rockwell C—65.4

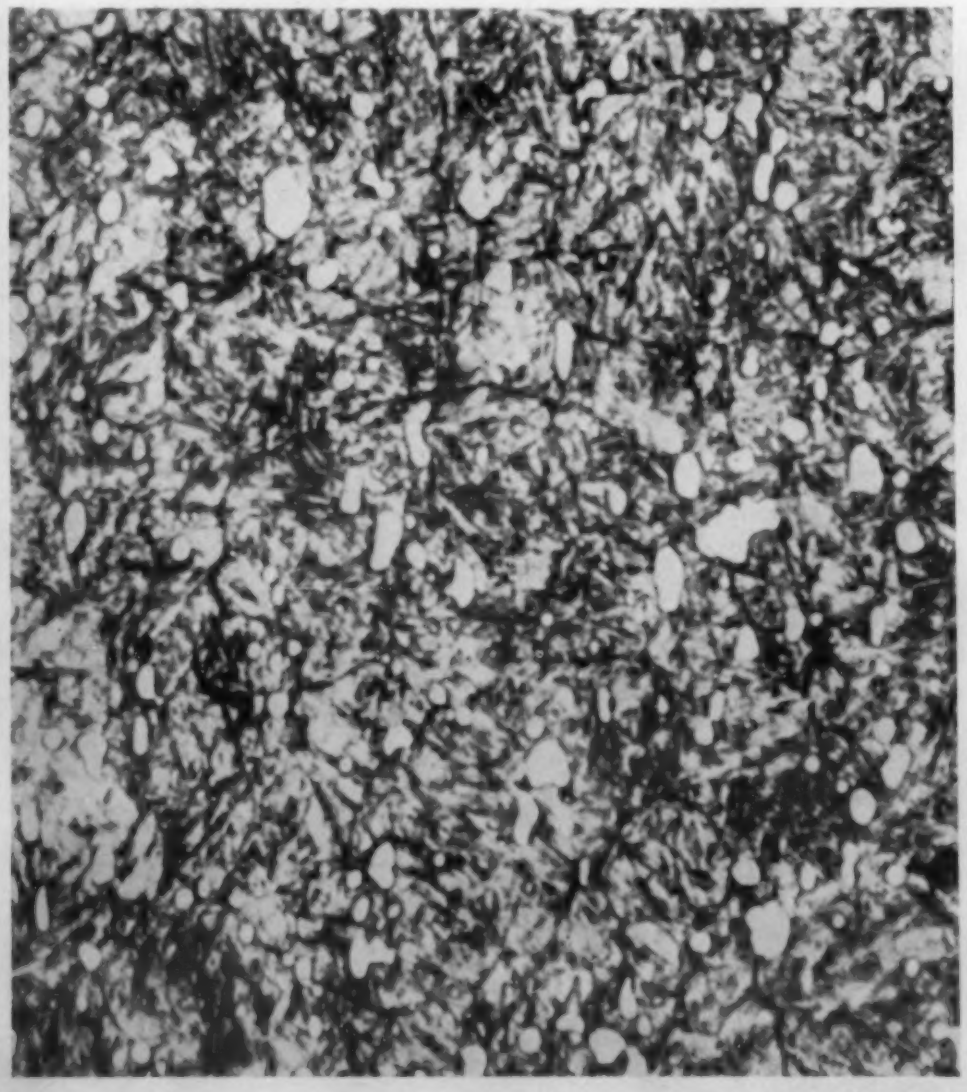
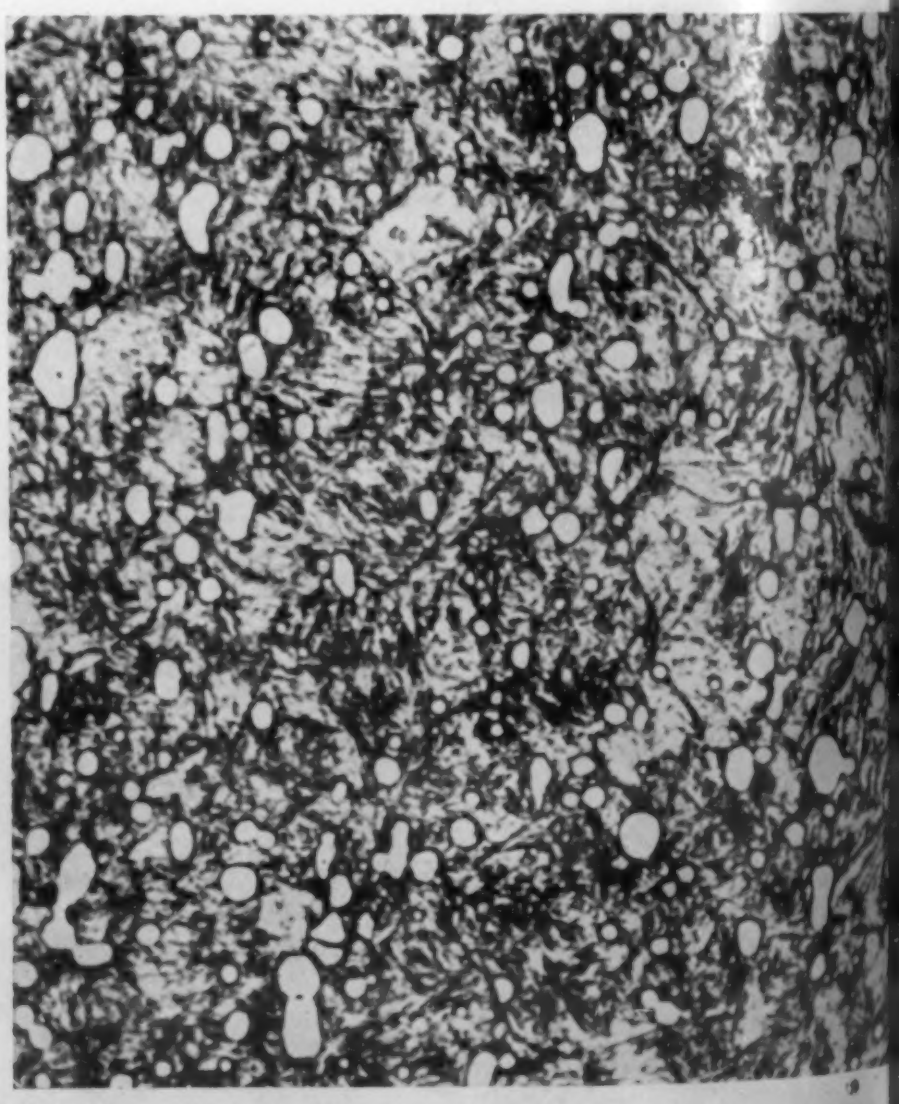
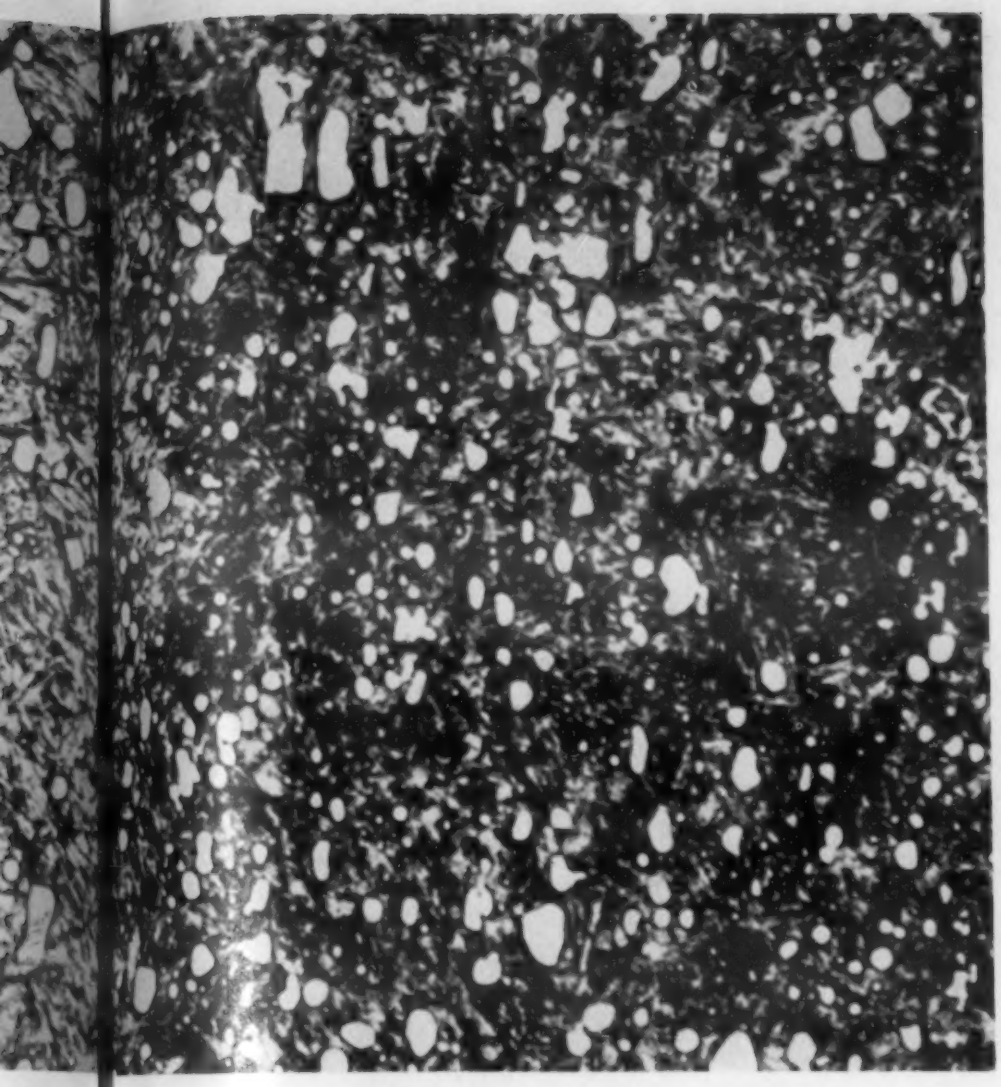


Fig. 4.—High Speed, Slightly Underhardened. X 2000. Etched for 2 mins. in 6% nital. Hardened at 2310 deg. F. for 30 secs. Tempe at 1040 deg. F. for 30 mins. Rockwell C—64.7





ig. 5.—Mo-Max, Considerably Underhardened. X 2000. Etched for 2½ mins. in 6% nital. Hardened at 2000 deg. F. for 30 secs. Tempered at 1040 deg. F. for 30 mins. Rockwell C—60.2

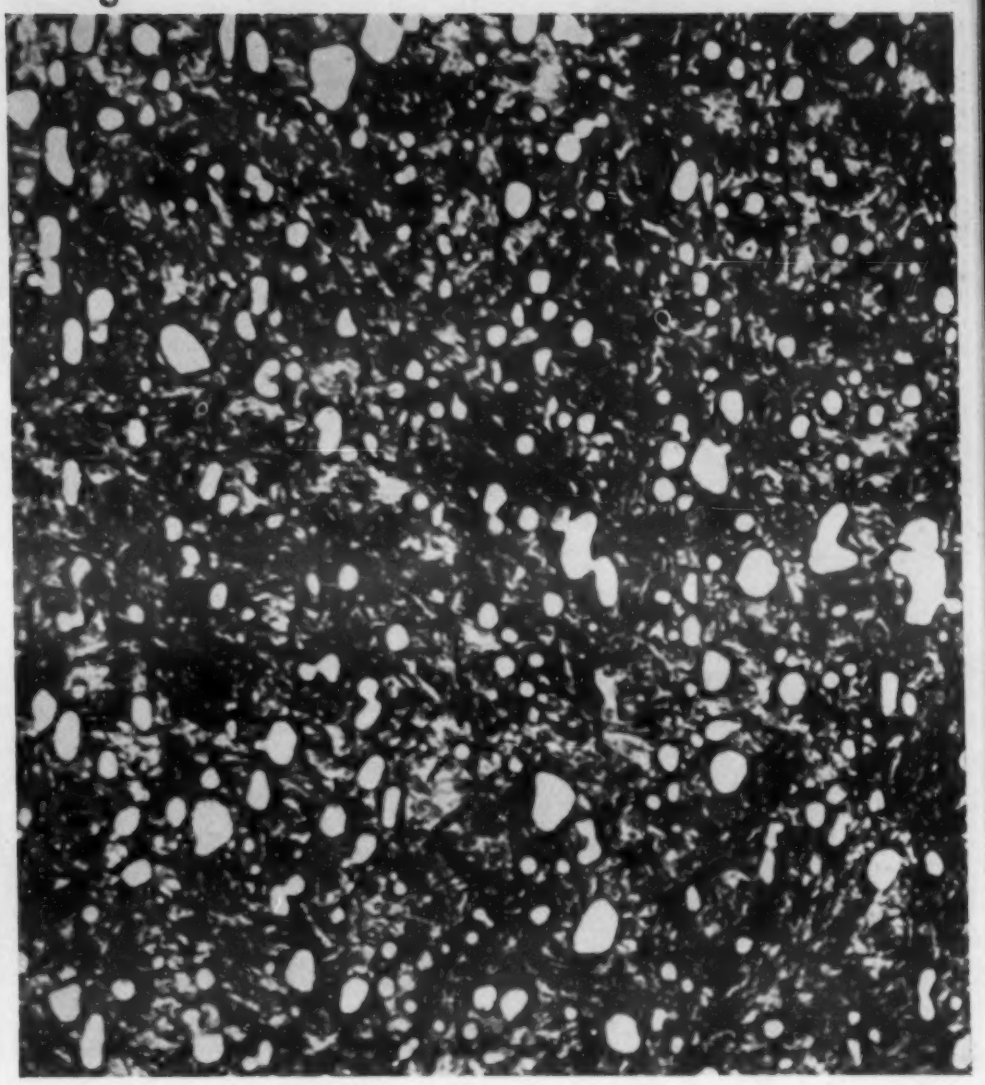
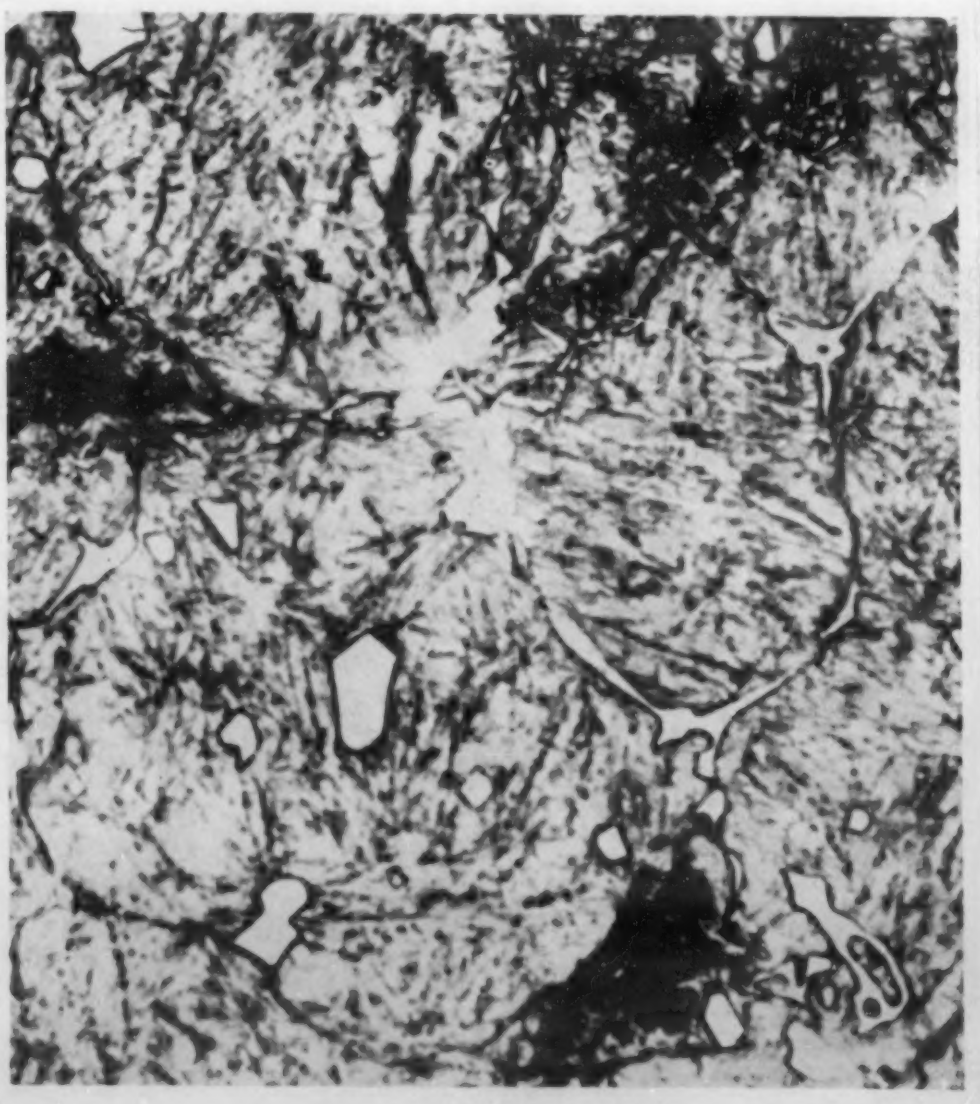


Fig. 6.—High Speed, Considerably Underhardened. X 2000. Etched for 2½ mins in 6% nital. Hardened at 2160 deg. F. for 30 secs. Tempered at 1040 deg. F. for 30 mins. Rockwell C—59.8

ig. 7.—Mo-Max, Overheated in Hardening. X 2000. Etched for 2½ mins. in 6% nital. Hardened at 2290 deg. F. for 30 secs. Tempered at 1040 deg. F. for 30 mins. Rockwell C—66.5

Fig. 8.—High Speed, Overheated in Hardening. X 2000. Etched for 2½ mins. in 6% nital. Hardened at 2420 deg. F. for 20 secs. Tempered at 1040 deg. F. for 30 mins. Rockwell C—65.5



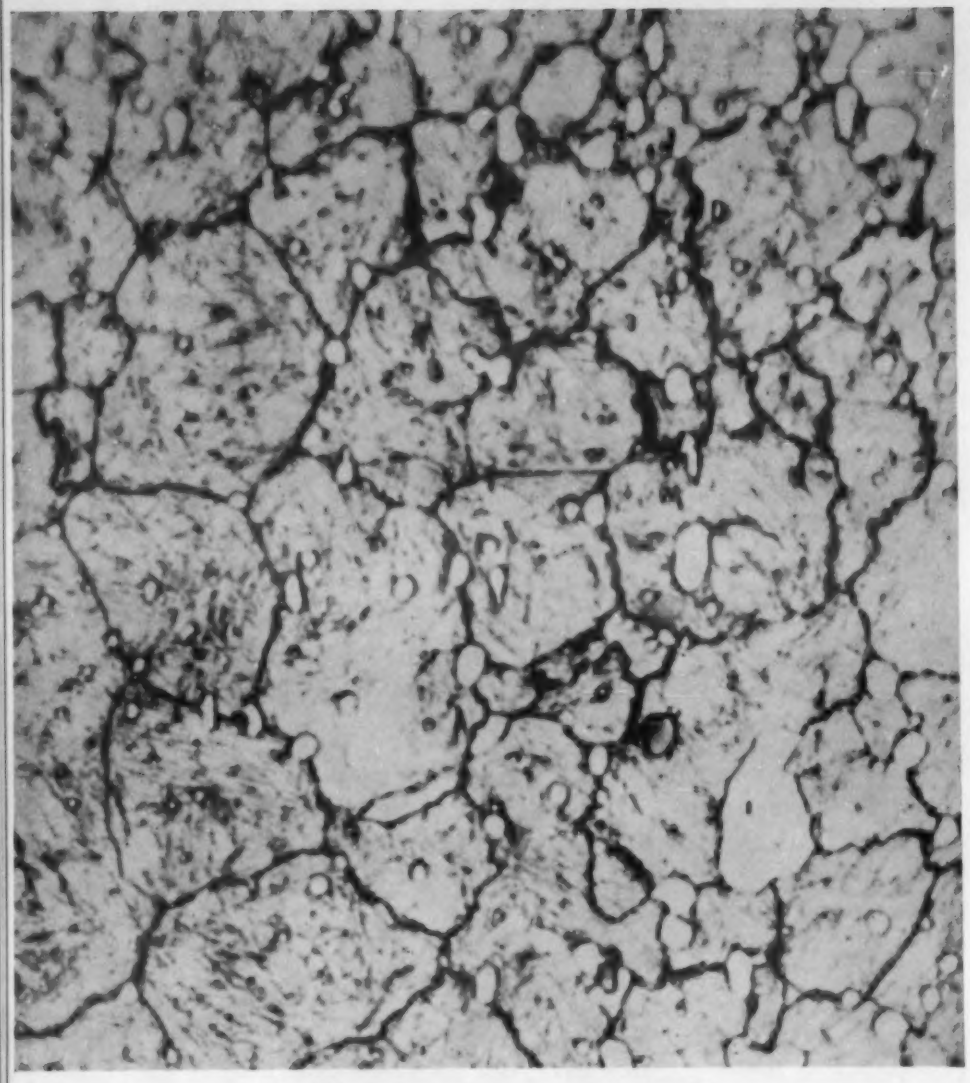


Fig. 9.—Mo-Max, Undertempered. X 2000. Etched for 2½ mins. in 6% nital. Hardened at 2220 deg. F. for 30 secs. Tempered at 940 deg. F. for 30 mins. Rockwell C—63.0

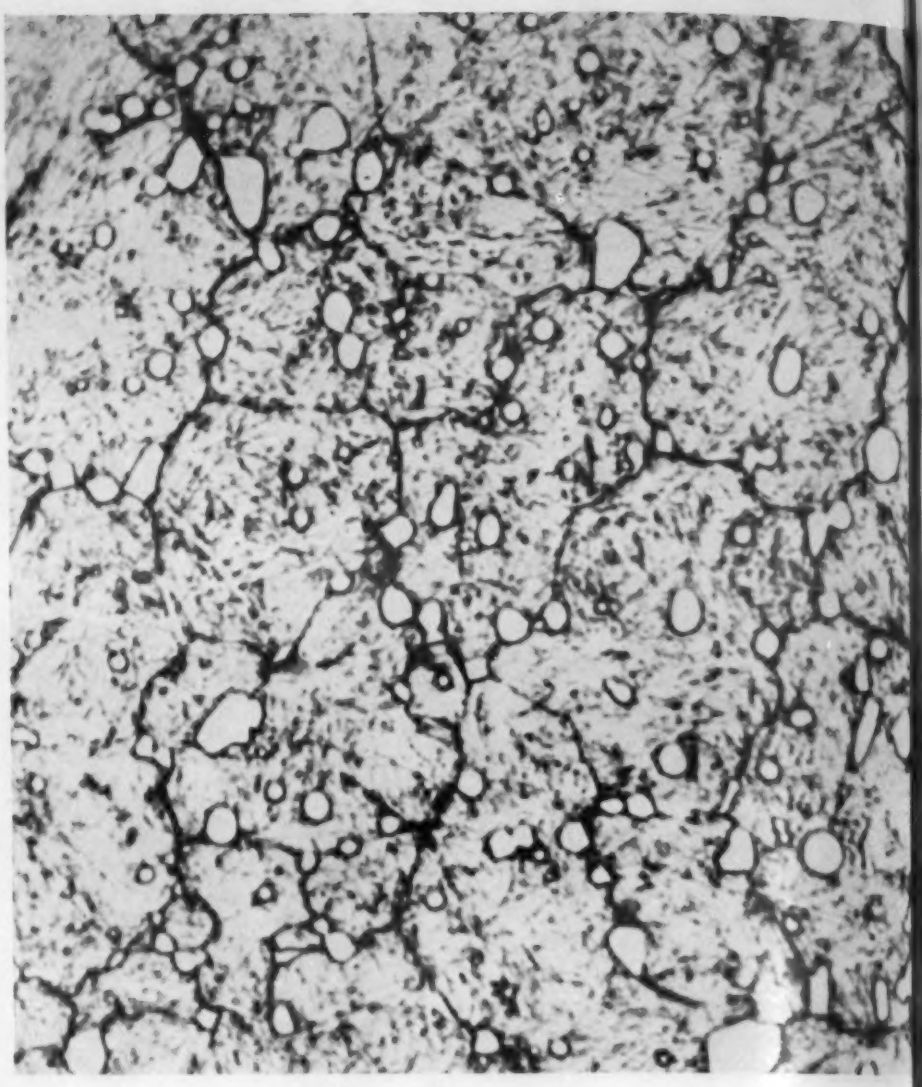
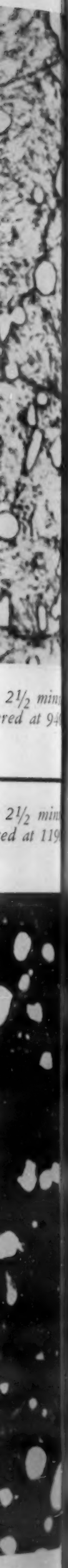


Fig. 10.—High Speed, Undertempered. X 2000. Etched for 2½ mins in 6% nital. Hardened at 2380 deg. F. for 30 secs. Tempered at 940 deg. F. for 30 mins. Rockwell C—63.5

Fig. 11.—Mo-Max, Overtempered. X 2000. Etched for 2½ mins. in 6% nital. Hardened at 2220 deg. F. for 30 secs. Tempered at 1190 deg. F. for 30 mins. Rockwell C—64.4

Fig. 12.—High Speed, Overtempered. X 2000. Etched for 2½ mins in 6% nital. Hardened at 2380 deg. F. for 30 secs. Tempered at 1190 deg. F. for 30 mins. Rockwell C—63.4



These structures and heat treatments might be called average for both Mo-Max and 18-4-1 high speed steels.

Slightly Underhardened—Figs. 3 and 4

In these micrographs the structures of Mo-Max and 18-4-1 are identical in every detail. This type of structure is distinguished from the normal structure by the fact that the austenitic grains are somewhat smaller and the boundaries less distinct. The martensitic needle structure is more vermiform and more richly outlined with dark troostite, and the carbides are somewhat more rounded in shape than are those in the normal structures. The cutting quality of tools with these structures is good and, in fact, is sometimes preferred where great toughness is desired.

Considerably Underhardened—Figs. 5 and 6

In these micrographs also, the Mo-Max and 18-4-1 steels exhibit identical details. This type of structure (Rockwell C hardness about 60) is distinguished by the fact that no austenitic grains are visible, the vermiform martensite is heavily outlined with troostite and there are many small rounded carbides visible.

Overheated in Hardening—Figs. 7 and 8

Since the hardening range for 18-4-1 is much closer to its melting point than is the corresponding hardening range for Mo-Max, the 18-4-1 steel was not overheated by the same amount that the Mo-Max was. The hardening temperatures of 2420 deg. F. for 18-4-1 (20 secs. soak) and 2290 deg. F. for Mo-Max (30 secs. soak) were chosen in order to produce badly overheated structures which would be roughly similar.

The martensitic needle structure is similar for both steels, although more heavily outlined with troostite in the Mo-Max structure.

The appearance of the carbides is the most conclusive proof of overheating. In the Mo-Max structure the carbides have formed an eutectic network outlining the large austenitic grains. This condition indicates a weak and brittle structure. In the 18-4-1 structure some large angular-shaped carbides are still visible while the remainder of the carbides are starting to form the skeleton-like eutectic envelopes around the large austenitic grains.

Considerable segregation has occurred in the matrix also, as evidenced by the dark patches visible in both micrographs.

Tools having such microstructures may be quite hard and have a high red-hardness, but they will invariably be weak and brittle and will chip easily on their cutting edges.

Undertempered—Figs. 9 and 10

Both Mo-Max and 18-4-1 show similar structures. The austenitic grain boundaries are quite distinct and the grains of moderate size.

The chief difference between this type of structure and the normal structure is that here the martensitic matrix etches very light in color and the martensitic needles are barely visible. No troostite formation is present to any great extent. Re-tempering these structures at 1040 deg F. will bring the Rockwell C hardness of the 18-4-1 up about 2 points and that of the Mo-Max up almost 4 points.

Overtempered—Figs. 11 and 12

Both Mo-Max and 18-4-1 show similar structures. These structures are characterized by white carbide particles in dark backgrounds. The 18-4-1 matrix is so heavily etched that very little martensitic structure is visible. The Mo-Max matrix shows some evidence of martensitic needles very heavily outlined with dark troostite. These structures represent hardness values somewhat below peak values, but toughness values considerably greater than those of the normal structures.

In general, it will be observed that variations in hardening temperature have chiefly affected the austenitic grain size, the shape of the needles in the martensitic matrix and the size, number and shape of the carbide particles. Variations in tempering, within the limits considered here, have affected chiefly the development of the troostite and hence, the color of the matrix. Overtempering also eliminates the austenitic grain boundaries because of the very rapid action of the etchant upon troostitic structures. In the above discussion the term troostitic has been used to describe that part of the microstructures in which carbon has been rejected from the martensite in the tempering process to form a constituent which darkens rapidly during etching with nital.

It should be noted that in all the structures the amount of visible carbide is approximately the same in both types of steel. This is interpreted as indicating that the 0.10% higher carbon content of the Mo-Max has gone into solution in the matrix.

The microstructures of Mo-Max and 18-4-1 are quite similar for corresponding heat treatments. In fact, it is practically impossible for a metallurgist to distinguish between them on structural grounds alone.

SHORT TIME

Creep Characteristics

OF STAINLESS STEELS

by S. I. Wolfson and A. M. Borzdika

An extended abstract, specially prepared for METALS AND ALLOYS, *of an article in Russian published in Kachestvennaia Stal, Vol. 4, No. 8-9, 1936, pages 8-12.*

BECAUSE OF THE GREAT INTEREST attached to the behavior of stainless steels at elevated temperatures, the determination of the properties of some of them under a static load and a study of their creep characteristics within the same temperature range were made. As a side issue of the problem, a comparison between the usual makes of nickel-chromium stainless steels and a chromium-manganese-tungsten steel proposed by A. M. Borzdika was effected.

The composition and properties at room temperature of the steels used in this investigation are given in Table I.

Creep investigation was conducted in the range 400-600 deg. C. using a lever apparatus and time intervals up to 140 hrs. The apparatus together with the auxiliary equipment for temperature regulation and elongation measurement were described fully in a previous paper by A. M. Borzdika.[1]

The data obtained in the present investigation are recorded in Figures 1 to 3. These curves illustrate creep characteristics of steels investigated in the early stages of loading. More detailed information on the subject is given in Table II.

The new steel D appears to have a considerably greater creep strength so that a load 2 to 3 times greater than for chromium-nickel and 3 to 4 times greater than for plain chromium steel is required to produce the same creep rate at any given temperature. The steel creeps rapidly at the beginning of load application, after which the creep curve flattens considerably. If the loads producing a creep rate of 10^{-6} per hr. after loading for 65 hrs. be plotted against temperature, as in Figure 4, the advantages of the new steel at higher temperatures are clearly demonstrated.

Short time tensile test results at elevated temperatures for steels B, C and D are given in Figures 5 and 6.

Though a certain scatter of results, due to differences in experimental conditions, could be observed, the results of

Table I.—Composition and Mechanical Properties at Room Temperature of Steels Investigated.

Steel	Composition, Per Cent C	Mn	Si	Ni	Cr	W	Ti	Tensile Strength, lbs./sq. in.	Elastic Limit, lbs./sq. in.	Elongation, %	Red. Area, %	Heat Treatment, deg. C.
A	0.10	0.45	0.3	0.5	12.5	...	...	56,900	28,450	25	74	Annealed 860
B	0.40	0.27	3.0	...	10.2	...	...	118,100	50,100	12.3	23.6	Annealed 860
C	0.20	...	...	5.75	19.2	...	...	124,200	28,000	45.5	57	Quenched 1050
D	0.40	8.9	0.36	...	17.0	2.2	0.28	117,300	27,400	26.5	29.5	Quenched 1100

Table II.—Average Creep Rates of Steels A, C and D.

Steel	Temperature, deg. C.	Load, lbs./sq. in.	Average Creep Rate in 10^{-7} per hr. in the range of: (hrs.) 5-10	10-20	25-35	24-48	40-70	70-100	100-140
A	400	28,500	130	55	20	16.6	15	16.6	13.3
	400	37,000	400	110	45	40	40	...	...
	500	11,400	...	80	20	16	13.3	13.3	...
	500	17,000	220	130	120	120	120	...	...
C	500	14,200	...	...	15.0	14.5	11.1	...	...
	500	11,400	93	25	8.3	5.9	...	...	...
	500	17,000	100	85	48.3	30.6	...	...	...
D	500	24,200	38	50	6.7	5.5	2.6	2.0	1.4
	500	27,000	...	...	8.3	3.5	2.0	1.6	1.6
	500	32,700	100	85	34.0	24.0	19.5	5.6	3.5
	600	24,200	108	54	33.0	23.0	26.0	...	...
	600	27,000	137	59	14.0	28.0	19.5	19.0	18.5

Table III.—Creep Strength of Steel D (Cr-Mn-W) Compared with Values for Cr-Ni-W Steels Found in the Literature. "Creep Strength" in each case is the load producing a creep rate of 10^{-6} per hr. at 65 hrs.

Type	Composition, Per Cent						Temperature, deg. C.	Creep Strength, lbs./sq. in.	Investigator
	C	Mn	Si	Ni	Cr	W			
WF 100	0.5	0.6	1.8	13	16	2.1	400	51,200	R. Mailänder
							500	31,300	
							600	18,500	
WF 100	...	..	...	13	16	2.5	600	19,900	Siebel & Ulrich [2]
18 and 8 + W	0.3	0.5	1.2	8	20	4.5	535	23,000	French et al [3]
							625	6,400	
Steel D (Cr-Mn-W)	0.4	8.9	0.36	..	17.0	2.2	500	28,500	Authors
							600	20,600	

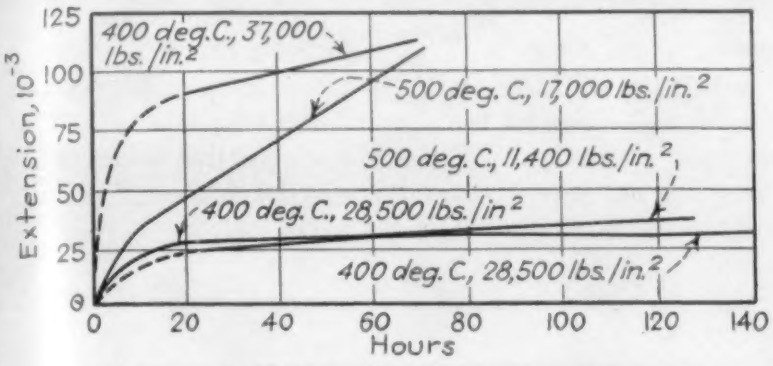


Fig. 1. Initial Creep Curves for Steel A.

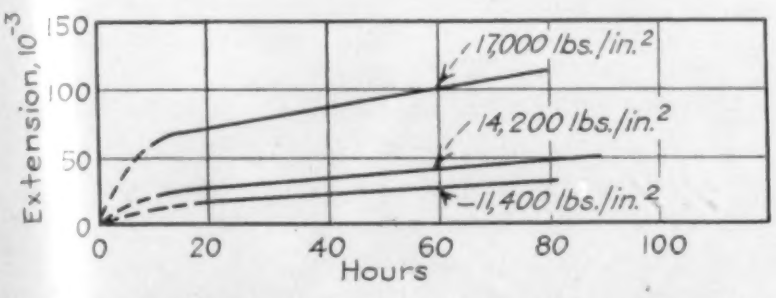


Fig. 2. Initial Creep Curves for Steel C. All tests at 500 deg. C.

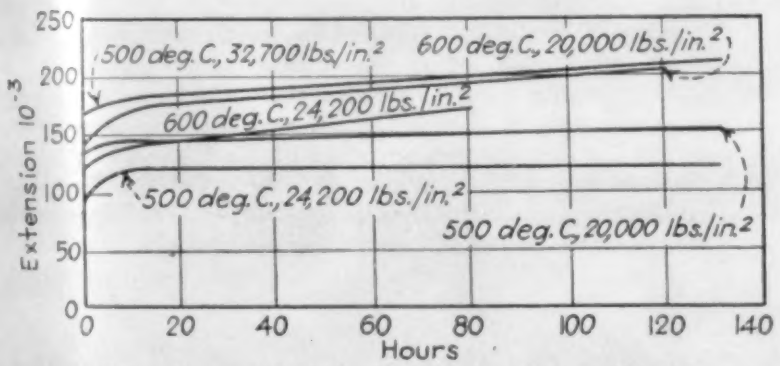

500 deg. C., 32,700 lbs./in.²
600 deg. C., 20,000 lbs./in.²
600 deg. C., 24,200 lbs./in.²
500 deg. C., 24,200 lbs./in.²
500 deg. C., 20,000 lbs./in.²
Extension 10⁻³
Hours

Fig. 3. Initial Creep Curves for Steel D.

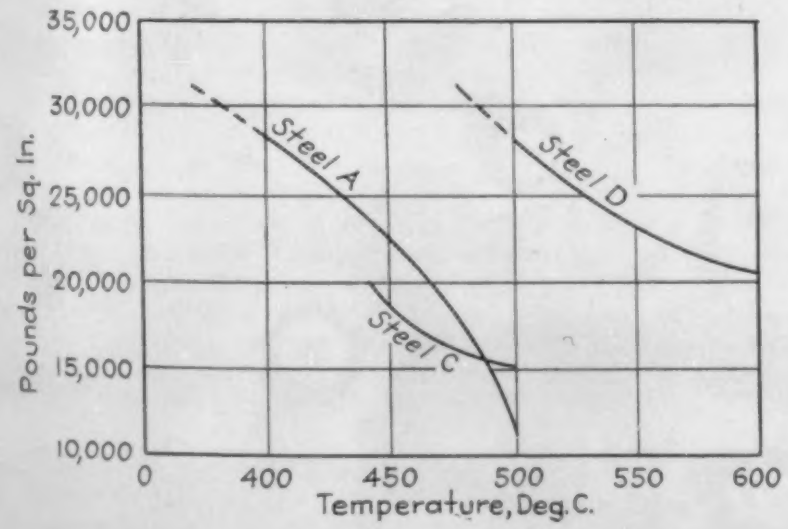


Fig. 4. Relation Between Creep Limit and Temperature for Steels A, C and D. Loads plotted are those producing a creep rate of 10^{-6} per hr. at 65 hrs.

creep determinations for steels A and C obtained in this experimental series are well within the range reported abroad by many investigators.

A comparison of the proposed steel with the WF 100 type made by Krupp, which contains 0.5 per cent C, 13

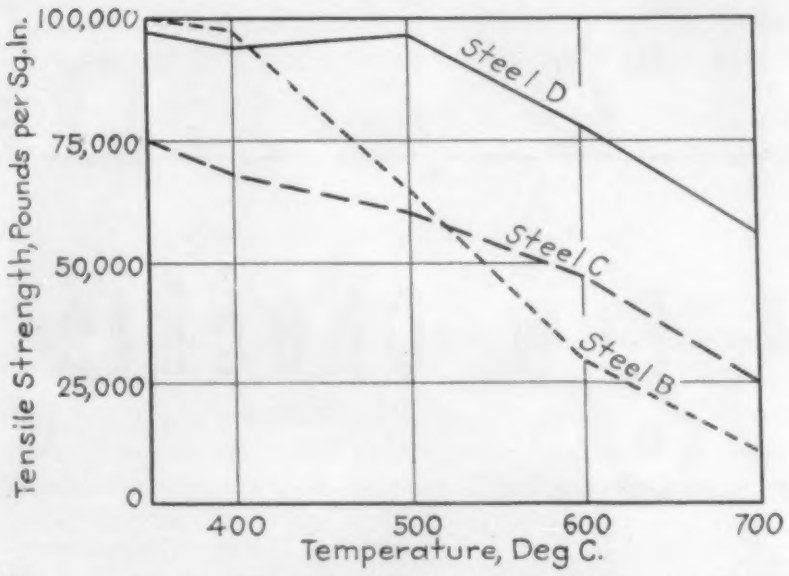


Fig. 5. Tensile Strength of Steels B, C and D as a Function of Temperature.

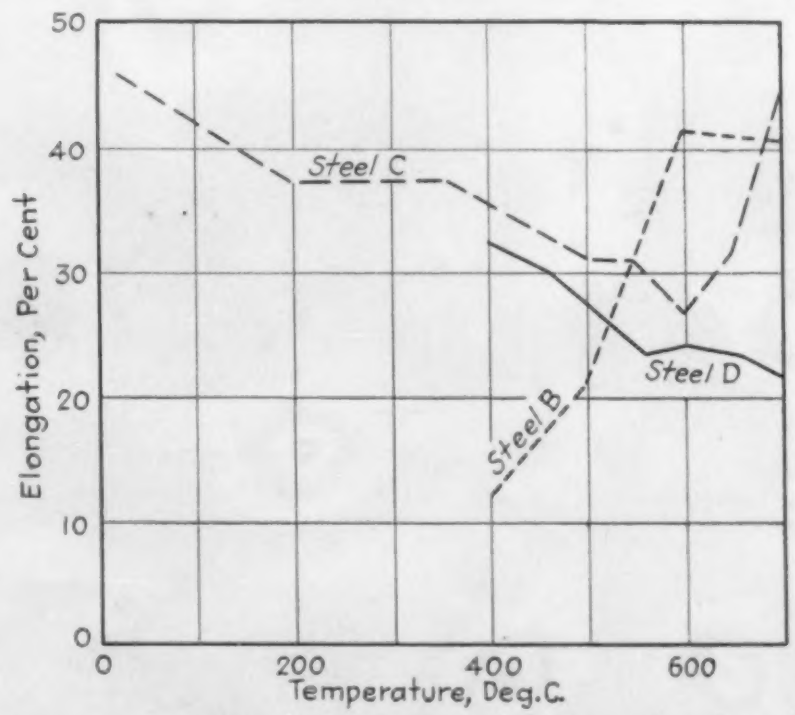


Fig. 6. Elongation of Steels B, C and D as a Function of Temperature.

per cent Ni, 15 per cent Cr and 2 per cent W and has creep characteristics about twice as good as of 18Cr-8Ni steels, showed that under the same conditions creep characteristics of the new steel are also twice as good as those of straight 18 and 8. The values obtained on this chromium-manganese-tungsten steel were close to those reported in

the literature on chromium-nickel-tungsten alloys, as indicated in Table III.

The data referring to WF 100 and to 18 Cr-8 Ni tungsten-bearing steels were obtained under particularly favorable conditions; an accelerated method was used for the former and exceptionally high W content was present in the latter. Nevertheless, the results recorded for the new steel are quite comparable with them, and indicate no deterioration in creep-resisting quality by replacing the Ni in Cr-Ni-W steels with Mn.

References

[1] A. M. Borzdika. *Zavodskaia Laboratoria*, No. 3, 1934.

[2] E. Siebel and M. Ulrich. *Zeitschrift Verein deutscher Ing.*, Vol. 76, 1932, pages 659-663.

[3] H. J. French, Wm. Kahlbaum and A. A. Peterson. *Journal of Research*, Bureau of Standards, Vol. 5, 1930, pages 125-183.

Supplementary Comment by H. W. Gillett

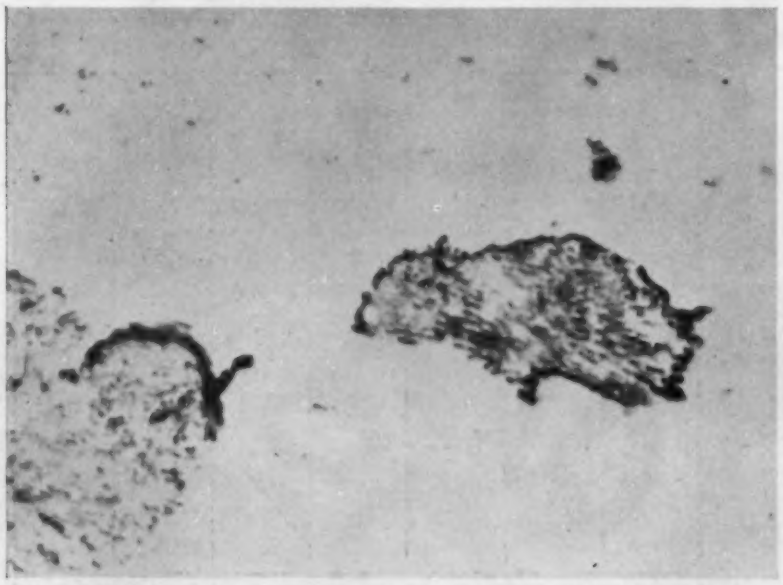
What the authors call "creep tests" and "creep limit" in the above have very little meaning because of the extremely short duration of the tests. The evidence as to load carrying ability can thus be taken as of qualitative interest only. Moreover the important questions of the stability of the alloy and its freedom from embrittlement in service are not considered. With such a high carbon and low titanium content stabilization by Ti is not to be expected.

While the evidence of the so-called creep tests adds but little to that given by the short-time high temperature tensile tests, it does have some such corroborative value, to indicate that the heat resistant alloys based on Cr and Mn deserve attention along with those based on Cr and Ni.

A Few Chuckles

Trademarks

What could be more appropriate than having an experimental heat of steel marked with a guinea pig! This is an un-retouched



pearlite area etched with alkaline sodium picrate. It is suggested that the animal may be about to eat something in the next clump. —C. E. Sims.

Abstract Metamorphosis — Reductio ad Absurdum?

(1) The original in Metals and Alloys:

The Cry of Tin. C. N. da C. Andrade & Bruce Chalmers. *Nature*, Vol. 129, Apr. 30, 1932, pp. 650-651; June 4, 1932, p. 833. The "cry" of Sn . . . . appears to be an accompaniment of twinning in both polycrystalline and single crystalline states. The sound probably indicates that twinning is propagated from layer to layer with a velocity of the order of that of sound. Possibly the phenomenon exists in other cases, but frequency may be too high for audibility.

(2) Semi-technical version:

Cry of tin due to the twinning of crystals.

(3) Non-technical version:

Birth of crystal twins causes tin to cry when bent.

(4) Final radio version:

The cry of a piece of metallic tin when bent has at last been identified by scientists as the anguished cry of motherhood. The bending motion forces the birth of twins among the internal crystals. Tin must thus be classed as a feminine metal, a classification which is confirmed by the capricious, changeable nature of tin in uniting readily with both acids and bases.—*B. W. Gonser.*

A Chuckle On Us!

I have enoyed a good many "chuckles" printed in Metals and Alloys. I also got a chuckle from Mr. Cone's article on "American Alloy Steels," Metals and Alloys, July 1937, page 192, right column, last sentence: "With the growing use of low alloy, *high electric* (italics mine) and the low copper steels, some of which are not now recognized."

Such a modest way to announce a new class of alloy steels, or haven't I recognized them when announced? How does Mr. Cone add the electricity in the furnace or in the ladle? How many Kilowatts per ton for *high electric* alloys? What per cent stays in the steel? Is the electric alloy a carbide former or a solid "solution"? Here is a good subject for a Doctor's thesis.—*R. E. Cramer.*

"High electric" for "high elastic" is one on us—Editors.

What Foreign Languages Do You Read?

On an application blank we saw the other day, the applicant replied to the question—"What foreign languages do you read?" as follows—"None; studied German two years." We couldn't rate him high as a linguist, but he scored for frankness.—H.W.G.

Refractories Testing—A Symposium

AN EXTENDED ABSTRACT

by John D. Sullivan

Battelle Memorial Institute,
Columbus, Ohio.

A SYMPOSIUM ON REFRACTORIES TESTING was presented at the Thirty-Ninth Annual Meeting, American Ceramic Society, New York, N. Y., March 23, 1937. Five of the seven papers presented at the symposium have been published.[1] Two papers entitled, "What Makes Testing of Refractories Difficult" by S. M. Phelps and "Apparatus and Equipment Used for Studying Properties of Refractory Materials at the National Bureau of Standards," by R. A. Heindl have not yet been published. This article abstracts some of the most important problems discussed at the symposium which are believed to be of interest to a large number of the readers of METALS AND ALLOYS.

Test Methods of A.S.T.M.

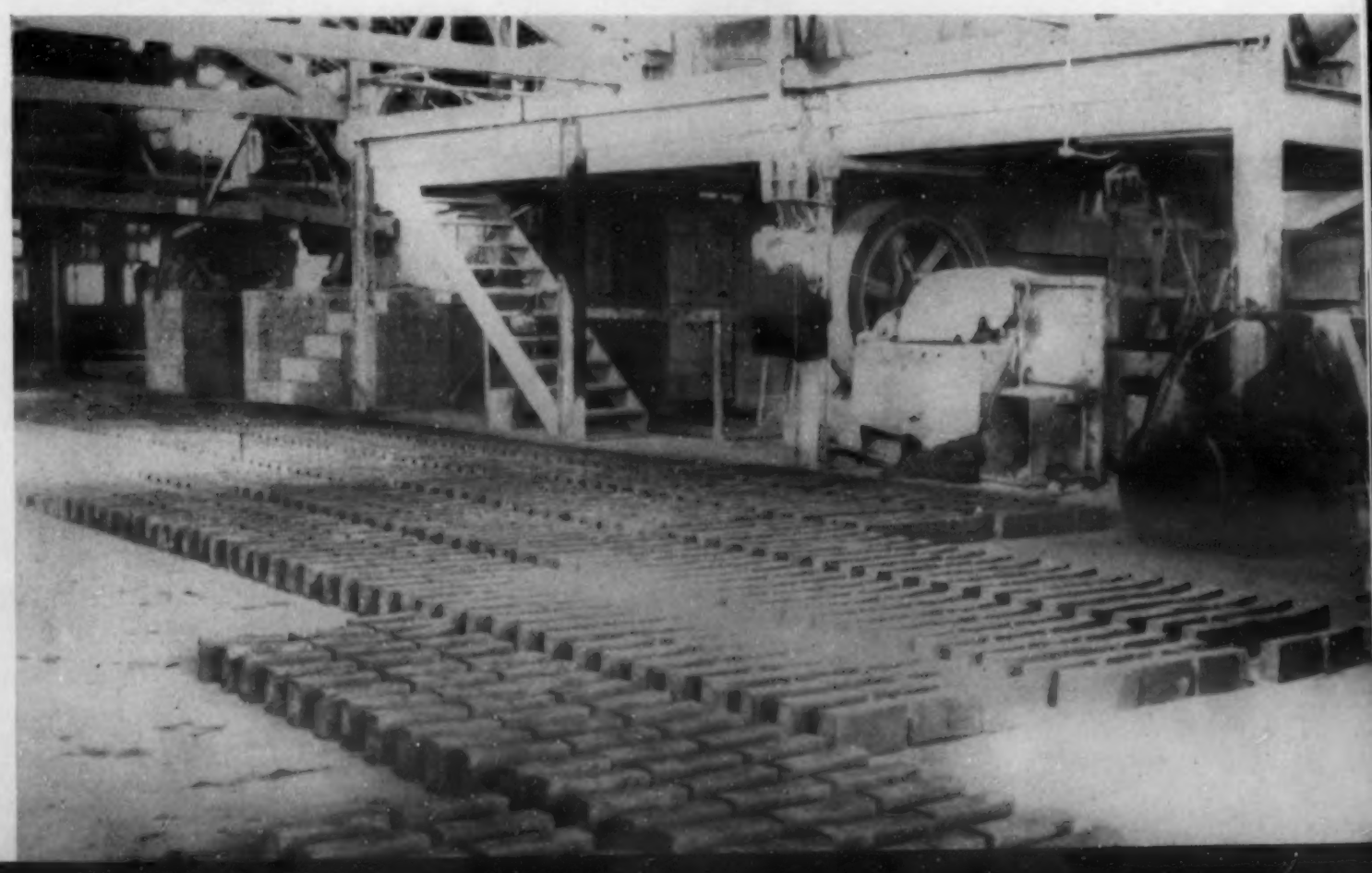
Phelps, in his paper, described testing methods used in the refractories industry, and stressed the problems encountered in the design of test methods for refractories to yield reproducible results. He pointed out the necessity of following details of testing procedure to obtain reliable results. Heindl, in his contribution, also stressed the necessity of careful attention to experimental details. He described various equipment and methods used at the National Bureau of Standards, including the interferometeric method of determining thermal expansion which has been described in detail elsewhere.[2] Because of their authoritative nature, the methods of testing of the American Society of Testing Materials should be followed when possible. The following methods of testing have been adopted by A.S.T.M.:

Test for Porosity and Permanent Volume Changes in Refractory Materials

Test for Particle Size of Ground Refractory Materials

Panel Test for Resistance of Refractory Brick to Thermal and Structural Spalling

Panel Test for Resistance to Thermal and Structural Spalling of Fireclay Brick for High Heat Duty Service



Drying Hand-Molded Shapes (Courtesy: Ironton Fire Brick Co.)

An Open Pit Clay Mine (Courtesy: A. P. Green Fire Brick Co.).

Panel Test for Resistance to Thermal and Structural Spalling of Super Duty Fireclay Brick
Test for Permanent Linear Change after Reheating of Refractory Brick
Test for Refractory Materials under Load at High Temperatures
Test for Softening Point of Fireclay Brick
Testing High-Temperature Heat Insulation (Compression, Flexure, Shrinkage)
Chemical Analysis of Refractory Materials
Chemical Analysis of Magnesite Refractories
Test for Cold Crushing Strength and Modulus of Rupture of Refractory Brick and Shapes

Phelps described in detail the panel or "Service Spalling" test of refractory brick to thermal and structural spalling, A.S.T.M. Designation C38-36. This test has also been described in detail elsewhere.[3] As applied to fireclay brick for high heat duty service, A.S.T.M. Designation C107-36, the test equipment consists of a preheating furnace, a spalling-heating furnace, air-mist ducts, and necessary handling equipment. A panel consists of two vertical rows of 9-in. straight brick laid up with kaolin having a pyrometric cone equivalent not below Standard Cone No. 34 (approximate softening temperature 1760 deg. C., 3200 deg. F.) and backed up with insulation, the thermal conductivity of which is such that the heat loss will be approximately 900 B.t.u. per sq. ft. per hr. The mean temperature of the insulation will be approximately 700 deg. C. (1292 deg. F.). The panel is preheated at a face temperature of 1600 deg. C. (2912 deg. F.) for 24 hrs.

When the preheating period is completed and before spalling begins the panel insulation is removed and the furnace is operated to obtain a temperature of 1400 deg. C. (2552 deg. F.). The spalling is conducted by alternately heating and cooling the panel for a period of 10 min. each, or a total cycle time of 20 min. Cooling is accomplished by means of an air-water mist blast, the air being supplied at 1400 cu. ft. per min. and the water at the rate of 2½ gal. during the first 8 min. of the cycle. No water is used during the last 2 min. After cooling, the panel is transferred to the hot furnace for reheating. The spalling treatment consists of 12 cycles after which the furnace is shut off and the panels given 2 additional cooling cycles without water mist. After dismantling the panel, the kaolin is scraped off with a trowel removing such portions of the brick that separate easily. The test brick are weighed to the closest 0.1 lb., and the loss in weight reported as percentage of original weight.

Navy Simulative Service Spalling Test

McGeary, in his paper, stated that of the several factors in the destruction of fireclay linings of Naval boilers, fusion and spalling are most important. Slagging is relatively unimportant since all the present boilers are oil-fired. It is of primary importance to have tests so that fireclay brick purchased will have maximum resistance to the temperature that may be encountered in service and maximum resistance to spalling action resulting from rapid changes in firing rates. In Naval practice the change in firing rate from 260,000 B.t.u. per cu. ft. furnace volume per hour to 26,000 or vice versa as fast as operators can shift burners is not uncommon. Standard wall construction of a Naval boiler is 4½ in. of dense fireclay brick, backed up with 2½ in. of 2500 deg. F. insulating brick, and 1 in. of 1500 deg. F. insulating block or board. Under full power conditions the brick exposed to flame must withstand 3000 deg. F. Under these conditions the mean temperatures are approximately as follows: Fireclay brick, 2650 deg. F.; insulating brick, 1700 deg. F., insulating board 650 deg. F. The casing temperature is about 200 deg. F.

Examination of samples of brick taken from boilers after continued use showed that the depth of vitrification was about 1 in. In order to obtain this depth, it was necessary to heat a panel to 2900 deg. F. for 24 hrs, followed by another 24-hr. period at 3000 deg. F., or vice versa.

The apparatus and test procedure used in the Navy Simulative Service Test were described by McGeary. He summarized the principal differences between the method of testing refractories by the Navy and the A.S.T.M. method as follows:

(1) Fireclay mortar is used by the Navy instead of kaolin to lay up the test brick, creating a spalling loss approximately three times as much as with kaolin.
(2) Somewhat less insulation is used in the Navy test.
(3) Oil fuel instead of gas fuel is used.
(4) The preheat test is run for 24 hrs. at 3000 deg. F. and 24 hrs. at 2900 deg. F., instead of 24 hrs. at 2912 deg. F. This increases the depth of vitrification, particularly in brick which are just on the border line in quality. Reducing the time to one run of 24 hrs. would have little effect upon the superior brick but would materially favor the brick of poorer quality.
(5) The spalling cycle is 20 mins. heating and 20 mins. cooling (400 mins. total time) with the insulation in place, instead of 10 mins. heating and 10 mins. cooling (240 mins. total time) with the insulation removed.
(6) The number of spalling cycles is 10 instead of 12.
(7) The cooling medium is atmospheric instead of air and water mist.
(8) Spalled portions are removed by thumb pressure instead of by scraping the sides of the brick with a trowel. This gives a spalling loss about two times as great as by scraping.

In the Navy spalling test high heat duty fireclay brick average about 18 per cent spalling loss while super duty fireclay brick average about 7 per cent.

Panel Spalling Tests on Insulating Firebrick

Resistance of insulating fire brick to spalling is believed by many to be a matter of great importance. Kerr, in his paper, discussed various methods currently used in testing insulating brick. The simplest test probably is that of placing a whole brick (9 by 4½ by 2½ in.) in a heated furnace and removing it to air-quench after a period of time. Another test is to air-quench the brick after a heating period in a furnace similar to the one used for water-dip spalling of fire brick. A third test consists of actually water-dipping the heated ends of the brick after a manner similar to the water-dip method sometimes used on dense brick. In this latter procedure the heating temperature has been varied according to the recommended temperature limit of the insulating brick. Panel-type spalling tests have also been used. Some of these are conducted without a preliminary pre-heat period. Some use air alone as the cooling medium. Other panel-type spalling tests have been made, whereby the heated face of the panel is sprayed with water to cool it.

Kerr's personal observations of the various tests were that in the first test, where the specimens are placed in a hot furnace and then are air-quenched, a crack usually occurred in the brick after several treatments. When the crack occurs so that the brick is divided into two pieces, roughly 4½ by 4½ by 2½ in., the test can no longer be continued on a fair basis since, in service, spalling ordinarily occurs on the face exposed to the heat. He tried, without success, to correlate test data obtained by this method with behavior in service. When the brick are heated on the ends only and air-quenched, the data are more reliable, although still not accurate enough in many cases to permit correlation with service behavior.

The panel spalling test developed by the Armstrong Cork Co. is summarized as follows:

Two test piers five brick high are built into a frame. Kaolin is used as a thin mortar in laying up the brick. The five test specimens of each brand are kept back about ¼ in. from the guard brick at the edges of the framework. No spring pressure is used.

For the preheat, the test panel is placed against the front of the furnace and a low flame is applied to dry out the assembly. This consumes several hours. When the brick are dry, the rear side of the panel is backed up with 4½ in. of insulating brick as closely similar to the test brick as possible. These "back-up" brick are placed to fit tightly without mortar. The furnace is then heated with as near neutral firing conditions as possible so that it attains a predetermined temperature in about 6 to 8 hrs. The furnace is then held at this temperature for a 24-hr. period to insure a thorough soaking on the face of the test panel under neutral or slightly oxidizing conditions. After the preheat period, the gas is shut off and the panel is allowed to cool in place, after which it is removed for examination and photographed. Any shrinkage or crack formations are noted.

After one such preheat period the brick are spalled by a cycle comprising 10 min. heating at 2000 deg. F. and 10 mins. cooling by air which blows on the face of the panel at the rate of 1400 cu. ft. per min. At the completion of 10 cycles of heating and cooling the brick are cooled and examined. The panel is dismantled, the spalled pieces are broken off by gentle thumb pressure, and the total loss is measured.

Kerr observed that the test usually produced a certain amount of spalling from the face of the panel, in unusual cases the face was sheared off to a depth of one inch, and in other cases the brick were cracked into six or more pieces. Some of the more resistant brick exhibited little change.

Kerr presented the following general conclusions from his study of thermal spalling of insulating brick:

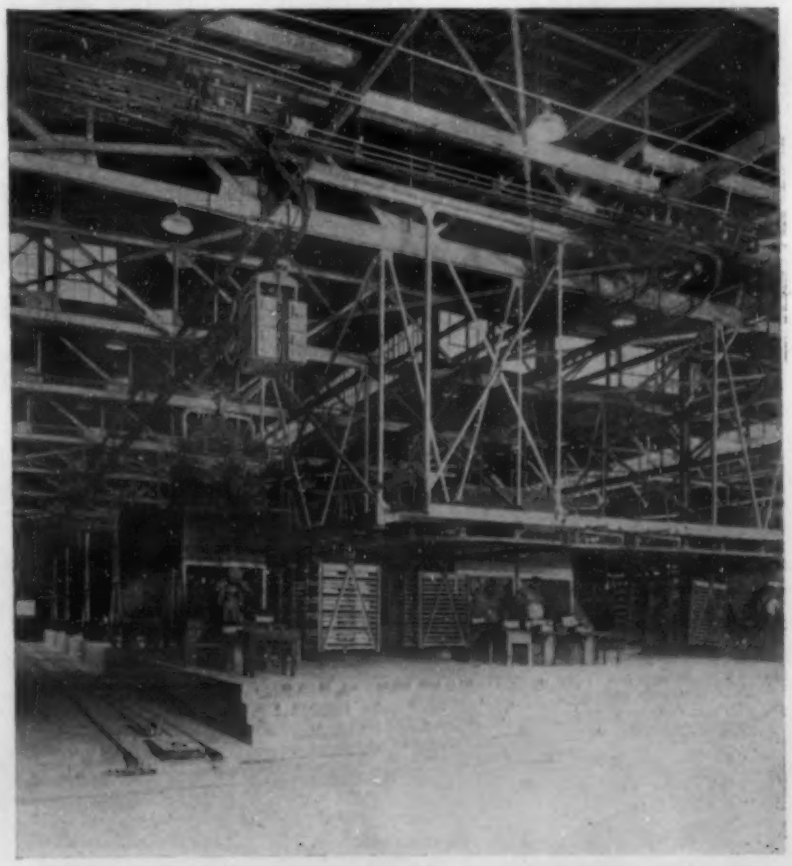
> The chemical constitution of the brick, for any definite temperature, is believed to be of less importance than some of the physical properties.
>
> A spongy structure is desirable. To be most effective, it must be coupled with good mechanical strength in the insulating fire brick.
>
> In general, the heavier brick exhibit better spalling resistance. No insulating fire brick have been found to withstand spalling so well as fireclay refractory brick at test temperatures of 2500 deg. F.
>
> Reducing conditions during the preheat period probably influence the spalling resistance adversely.

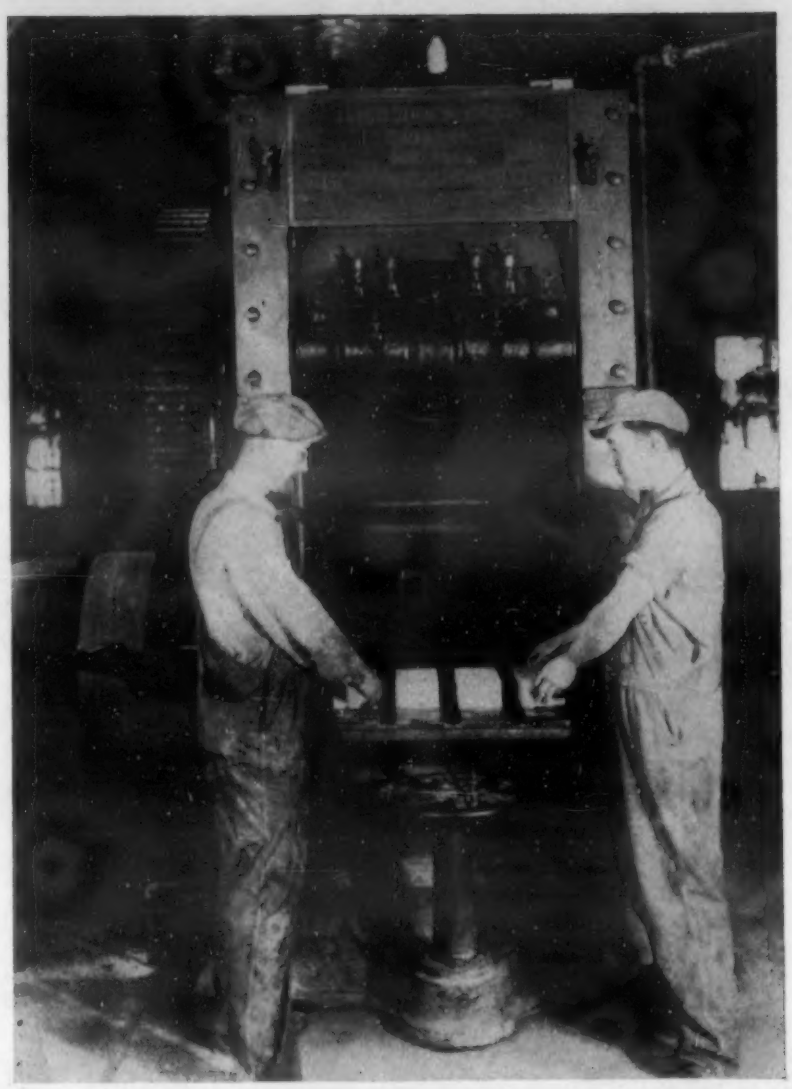
The spalling test for high-temperature insulating brick used by Kerr at least divides the materials into three general classes, (1) good resistance to spalling, (2) medium resistance to spalling, and (3) poor resistance to spalling.

Methods of Testing Insulating Refractories

Perhaps the most important requisite of insulation is low thermal conductivity, although in the case of insulating firebrick used in construction of intermittently operated furnaces thermal capacity may be of equal importance. Although considerable work has been done for years by various investigators, the agreement between different laboratories on the measured thermal conductivity of refractory materials is exceptionally poor. Nichols[4] has summarized the results obtained by different investigators on tests on the same lots of fireclay and silica brick. A later co-

Making Hand-Molded Shapes (Courtesy: A. P. Green Fire Brick Co.)



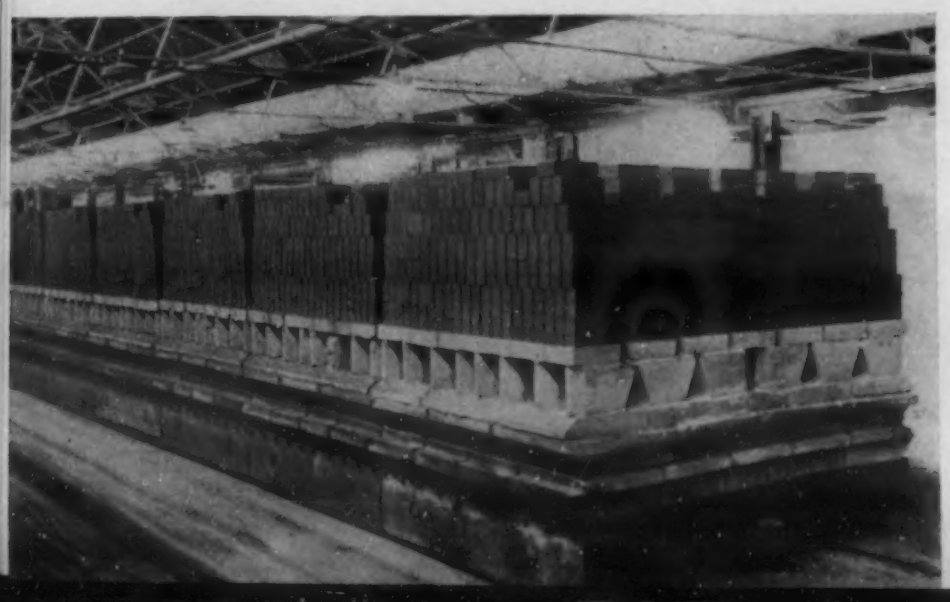


A Dry Press (Courtesy: Ironton Fire Brick Co.)

operative study sponsored by A.S.T.M. on thermal conductivity of carefully selected insulating firebrick showed about the same order of agreement. An investigation is under way at the National Bureau of Standards to attempt to determine the reason for different results by different test methods, and to develop a standard test procedure. The results of this investigation are awaited eagerly by the refractories industry.

The only A.S.T.M. test method for insulating refractories is the Tentative Method of Testing High Temperature Heat Insulation, Designation C93-34T. The methods cover compression, flexure or cross-bending, and shrinkage tests. The crushing strength of insulating brick is low; so the A.S.T.M. test provides that the test specimen shall be compressed to a deformation of 5 per cent of the original thickness unless failure occurs previously, and the maximum load obtained reported. Reheat shrinkage is obtained by heating the test specimen to a predetermined temperature

A Tunnel Car (Courtesy: A. J. Lavino Co.)



in not less than 3 hrs., and soaking at that temperature for 24 hrs.

Porosity of insulating brick may be determined in three ways. The first of these is by the determination of true specific gravity, weight, and bulk volume; the second, by boiling in water with determination of dry, saturated, and suspended weight; the third, by the use of a gas-expansion porosimeter. If the later equipment is available, a closer approximation of the true porosity can be obtained by this method than by the second method of boiling in water. Rueckel concluded, however, that there is slight correlation between porosity and other properties of insulating brick, and that brick density is of much greater practical value.

Permeability is usually expressed as the quantity of gas flowing through a specimen per square inch of area per inch of thickness in one second under a definite pressure differential. Equipment used for this test varies greatly but in general consists of (1) a container which seals the sides of the specimen to prevent lateral air flow; (2) a means of moving gas through the specimens which may be forced through as compressed gas or drawn through by a negative pressure; (3) a meter for measuring the quantity of gas flowing per unit time; and (4) a differential pressure gage. Rueckel stated the permeability of refractories to gases decreases as the temperature of the gas increases, that cement coatings applied to the surface of insulating refractories decreased the permeability of gases only about 50 per cent, and that, while permeability of insulating refractories may be of importance in a few isolated cases where high furnace pressures are maintained, in most such cases leakage is prevented by means of a steel shell.

Most insulating refractories show poor resistance to deformation under load at high temperatures, but in service there is no indication of failure of light weight brick due to poor load-bearing ability at elevated temperatures.

Insulating fire brick are in their infancy, and a great deal more work must be done in developing standard testing methods.

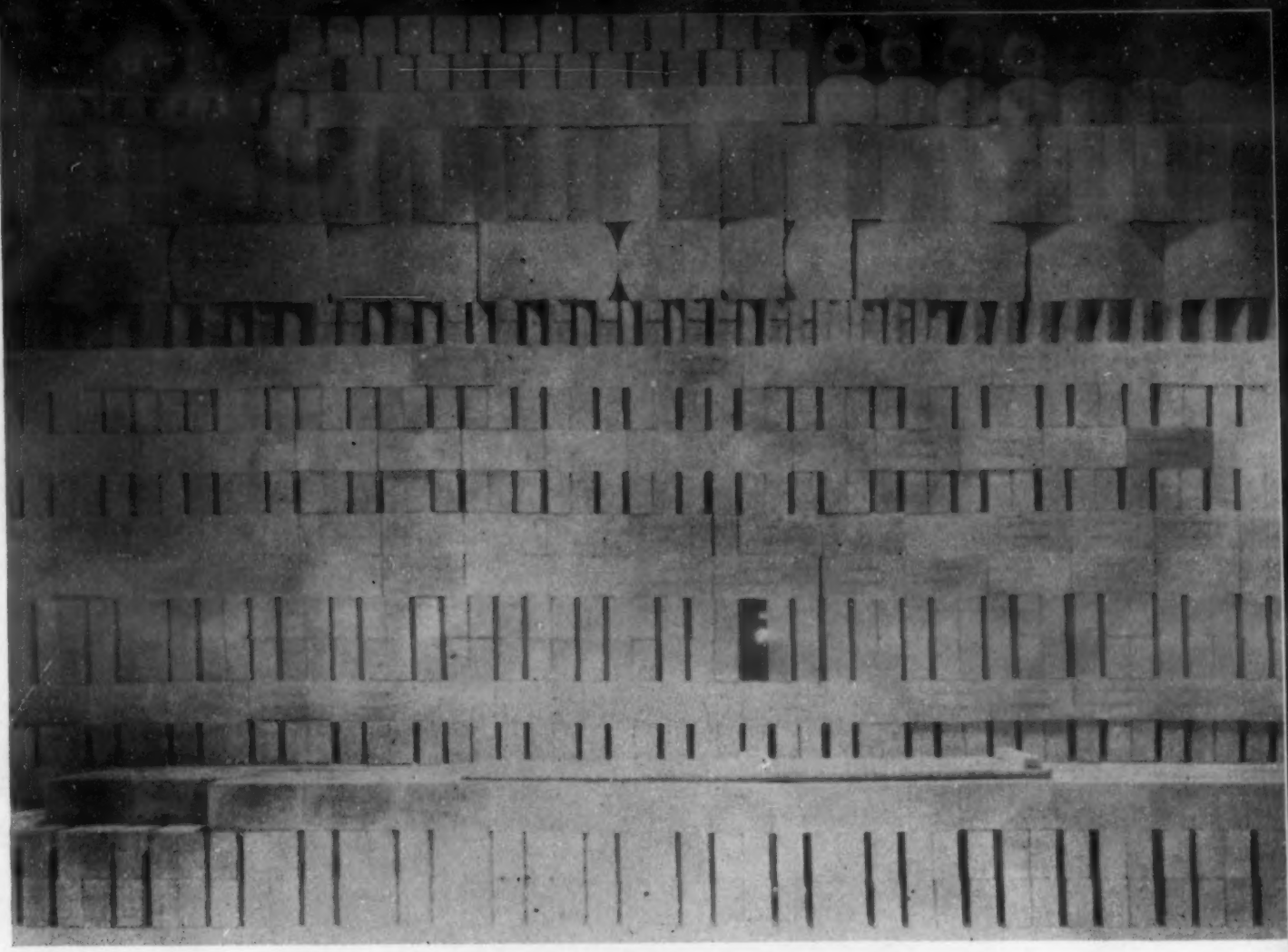
Practical Service Testing of Refractories

Callinan and Soler, in their paper, pointed out the relationship between refractory service and the economics of steel production. In some plants furnace time is rated at $1 per hr. per ton capacity; so even minor delays for repairs or replacements are expensive. Another economic aspect is the effect of refractories on quality of steel, which may be affected by direct contamination, by physical or chemical effect, or by their effect on the mechanical manipulation either of the molten or hot plastic steel.

An interesting example was cited. A nonmetallic fireclay inclusion no larger than a pin-head may ruin a gear and the cutter tool. The authors feel that service tests should be used to supplement and not to replace laboratory testing. Service testing is an individual problem in each plant for conditions vary considerably. Furnace design, combustion conditions, temperatures, and the manner of processing in the furnace affect the brick. These facts must be kept in mind when correlating and studying service-test data. Each alloy steel plant has its own particular problems, and consequently, satisfactory refractory life in one plant does not assure equally good results in another.

The service tests used at the Timken Roller Bearing Co., Steel and Tube Division, were discussed.

A Loaded Periodic Kiln (Courtesy: Ironton Fire Brick Co.)



A preliminary inspection is given all refractory shipments before the material is unloaded, noting general appearance, texture, warpage, and condition after shipping. After unloading, samples are inspected in the laboratory for uniformity of texture, lamination, warpage, and trueness of dimensions. If necessary, certain laboratory tests are made. Regular first quality brick for ordinary service may be given a pyrometric cone equivalent (P.C.E.) test and a combined reheat and pellet slag test. If these results are satisfactory, the brick are further checked in service. When the service test is completed, the brick are again examined closely and often a petrographic analysis is made.

Open-hearth furnaces lend themselves quite readily to service tests because there are several places where brick may be installed for testing without serious danger of interrupting furnace operation. Burner ports, bulkheads, slag pockets, and checker chambers offer excellent opportunities for test installations. The resistance of neutral or basic brick to slag erosion at high temperatures may be tested easily in burner ports. End-wall bulkheads provide a severe test for silica, basic, neutral, and super-duty brick which are designed for resistance to slagging at high temperatures and erosion by slag-laded flame and gases. A special advantage of this location is that test brick may be removed at any time for further study without interfering with the furnace campaign. The false inner wall and bulkheads of slag pockets offer a good position for testing the effect of slag penetration on silica and fireclay brick. Even though temperatures may not be so high in this location as in the upper furnace sections, the test brick are subjected to a long soaking action while exposed to the slag and heat. Service tests are easily made in the upper courses of checker chambers. In a well-designed checker chamber, failure of the brick is usually due to slag action, and it should be noted that temperature and the presence of a reducing atmosphere may increase the severity of the action. Here again, test specimens can be easily observed or removed for inspection.

Considerable difference exists between electric furnace conditions and those in open-hearths. Temperatures here are sharper and more concentrated while a reducing slag is encountered during the greater part of the heat. The furnace atmosphere is reducing and a comparatively high pressure is built up in the furnace. Flux-laden gases rise through the electrode holes, subjecting the ring brick to severe slag erosion. The separately turned ring arch around each electrode is subject to the most severe service of any point in the furnace roof. Here are encountered the problems of slag attack and spalling, and as the brick can be watched throughout the roof campaign, these rings offer an ideal spot for service tests, particularly as the roof may be removed before complete failure occurs. An electric furnace back wall above the tap hole is subjected to attack by liquid slag and steel when the furnace is tilted for tapping. During the heating period, this portion of the furnace is subject to severe spalling conditions. Basic brick can be tested in this location, as their condition may be observed through the charging door in the front wall of the furnace.

It is comparatively easy to test pouring-pit refractories, since, with the exception of ladle brick, they are used only during a single heat. Service tests furnish valuable information on nozzles, sleeves, stoppers, plugs, hot tops, and ladle brick, and the results have an important effect on the quality of the steel. Action of the steel on these refrac-

A Dry Pan.

tories being particularly severe, there are great possibilities of entraining nonmetallic inclusions from these sources. Such inclusions have the least time to rise out of the steel because solidification takes place soon after pouring. Double pour baskets offer an excellent opportunity for subjecting nozzles to service tests as the ferrostatic head is held constant and the two nozzles may be compared under identical conditions. In case of failure, pouring can be continued from the main ladle without losing any metal.

Callinan and Soler summarized their observations on service testing of refractories in an alloy steel plant as follows:

> Good judgment must be used in evaluating service test data and applying the results to other applications. Casual visual inspection is risky, for what may apparently be a minor item in a test application may be of critical importance in another case where conditions are more severe. Single tests are also not dependable; e.g., what may be a good ladle brick in a small ladle used for a certain type of steel may prove entirely unsuited for use in a larger ladle used for several types of steel. Variations in furnace practice in making different kinds of steel may further complicate the problem of evaluating the furnace refractories. Consequently, if preliminary laboratory and service tests indicate that a refractory may be satisfactory, testing should be continued over a period of weeks or even months so as to include a wider range of service conditions. Changes should be made with caution, for the quality of alloy steel depends in a large measure upon the refractories used in the furnaces, ladles, and ingot molds.

Correlate Laboratory and Service Tests

The papers and discussions at the Symposium stressed the importance of and interest in refractories testing. Laboratory tests are important in developing new products and in evaluating products to be used in industry. Specifications have been written for many refractory products, and in most cases tests have been devised to determine if the products meet the specifications. With the development of new products and with increasingly severer service conditions new tests must be developed. Wherever possible laboratory tests should simulate as nearly as possible service conditions. Service tests are necessary as a follow-up, and the correlation between laboratory and service tests should be established. With the application of scientific principles to the manufacture of refractory materials more and more attention is being paid to examination with the petrographic microscope and X-ray. Some work is being done at the present time on use of electron diffraction as an additional tool for examination of ceramic materials.

The A.S.T.M. issued a new manual on refractory materials in October, 1937, covering specifications, methods of testing, definitions, standard samples, test data manual, and industrial surveys. This manual is recommended to those interested in refractories testing.[5]

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[4] P. Nichols. "Determination of Thermal Conductivity of Refractories —Report for A.S.T.M. Subcommittee C-8," *Bull Am. Ceram. Soc.*, Vol. 15, 1936, No. 2, pp. 37-51.
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THE METALLURGICAL STORY OF

Ford Brake Drums

by Edwin F. Cone

THERE HAVE BEEN, AND STILL ARE, several types of brake drums, either in one piece or two, for automobiles. Of course the braking equipment of a car must be strong and dependable.

Until some years ago it was the ordinary practice of the builders of the lighter types of passenger automobiles to use a low carbon pressed steel drum. There soon developed defects in this. It was soft and not rigid enough to retain its roundness or shape, often being distorted into an egg shape. It was also subject to scoring. But this was not a serious problem under the old conditions. With the advent, however, of greater operating speeds, it became necessary to improve the brakes. This article is the metallurgical story of brake drums as developed by the Ford Motor Co.

Cast Drums Displace Pressed

Under the new operating conditions, the pressed steel drum was inadequate. In considering a substitute for this, two things had to be considered: Suitability of the braking surface, and strength. About the same time there developed a trend toward a change in design—the use of larger inner hubs and very short spoked wheels. Before a change in design, it was easy enough to use a braking ring of low strength and some type of forged steel or malleable iron hub, as there was enough wheel to take the load of the car. This made the two-piece drum—a hub and a brake ring.

On the rear wheels a gray iron ring with a forged hub was used and on the front a malleable ring and hub cast integral was tried. This chromium-nickel gray iron ring on the rear wheels was very satisfactory as a braking surface and adequate for strength with that design. The malleable ring and hub at the front was all right in every way except for its unsatisfactory braking surface. This can be easily appreciated in view of the experience with the pressed drum—the structure of the pressed drum was almost 100 per cent ferrite and the malleable iron was ferrite and graphite, but not enough graphite to improve the wearing qualities appreciably.

The trend in design was then changed to an even larger hub and no wheel whatsoever. This made it necessary to either use a very large forged hub and gray iron ring or to cast a material that could be suitable for a

brake surface and strong enough for the hub and part of the wheel.

Chemical Specifications Finally Adopted

Experience had demonstrated that malleable iron was unsatisfactory for braking surfaces. Due to the extensive experience of Ford metallurgists in casting other high carbon steels such as crankshafts, pistons, etc., previously described in articles in METALS AND ALLOYS, it proved rather simple to adopt a slight variation of these compositions for brake drums.

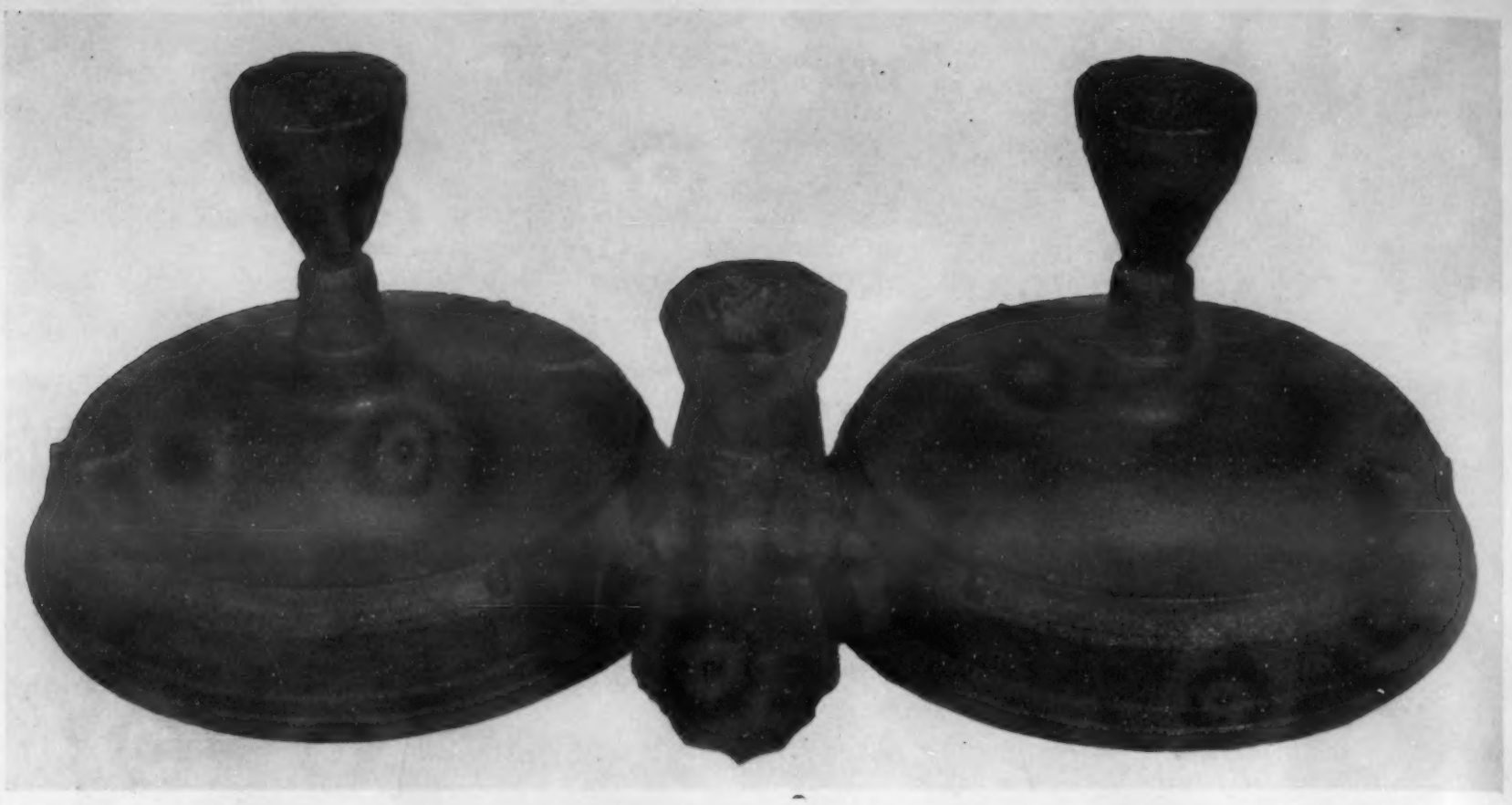
After many trials and investigations, the following chemical specifications were adopted for brake drums:

	Per Cent
Carbon	1.55 to 1.70
Silicon	0.90 to 1.10
Copper	2.00 to 2.25
Manganese	0.70 to 0.90
Phosphorus	0.10 Max.
Sulphur	0.08 Max.

All brake drums for Ford V-8 cars are now made strictly to these specifications.

Heat Treatment and Physical Properties

Before using, these castings have to be subjected to careful heat treatment. This is stipulated as follows:



The Brake Drums Are Cast in Pairs. This is as they look after coming out of the mold. They were poured with Brackelsberg metal. Courtesy: Kelsey-Hayes Wheel Co., Detroit.

Heat to 1650 deg. F. and hold for 30 min.; cool rapidly to 1400 deg. F., and then cool at the rate of 90 deg. per hr. to 1200 deg. F. This is followed by cooling in 1 hr. to 1000 deg. F.

The Brinell hardness then is 187 to 241. The physical properties of this material thus heat treated are as follows according to two tests, representative of many.

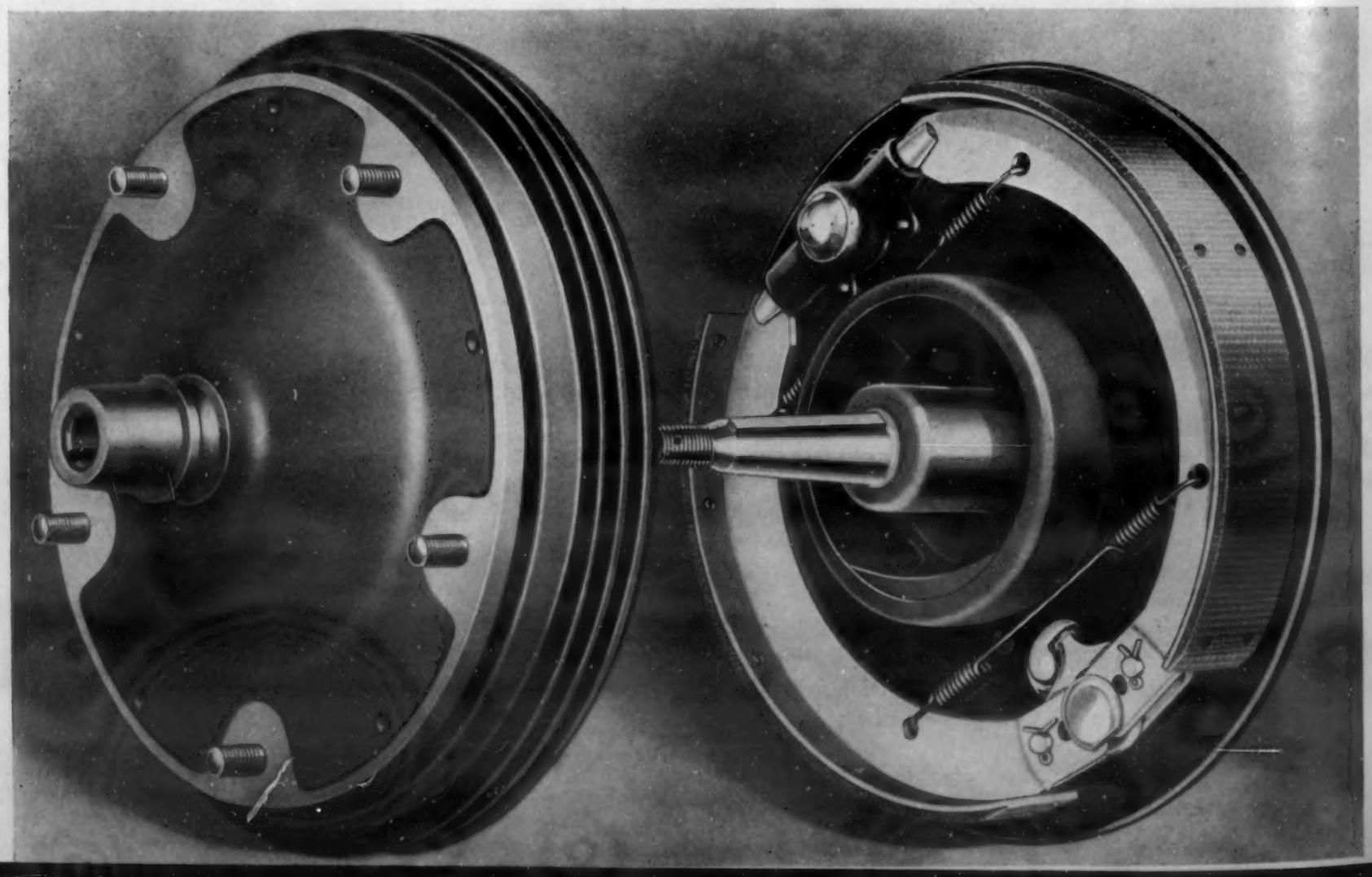
	1.	2.
Elastic limit lbs. per sq. in. ...	69,400	70,300
Tensile strength lbs. per sq. in.	85,600	85,100
Elong. in 2 in., %	7.07	7.00
Brinell	217	223

The heat treatment specified is carried out in gas-fired continuous furnaces of the roller rail type or in gas-fired pusher type furnaces. The structure of this alloy, as cast and after heat treatment, is shown by the photomicrographs.

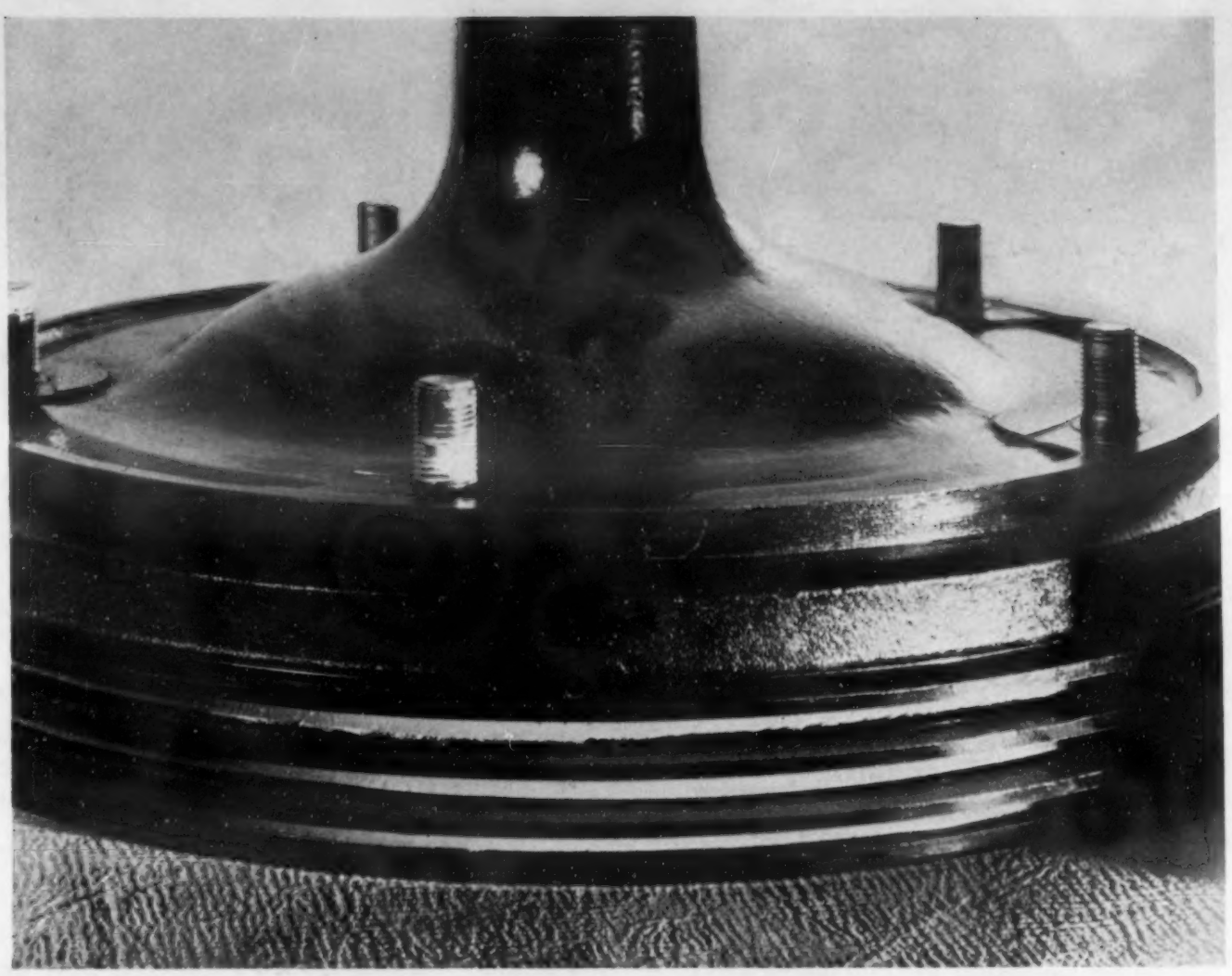
Obtaining Desired Structure

It has been found by Ford metallurgists that the ideal microstructure for a steel braking surface is a lamellar pearlite with graphite distribution, primary in the case of gray iron and secondary in the case of metal of this special analysis. Therefore the analysis specified is one that can be economically cast and normalized to produce the structure desired.

How the Brake Drum is Applied.



Another View of the Application of the Brake Drum.



The carbon is held well under the malleable iron range and just in the steel range. It should be as high as possible for casting reasons and not so high as to anneal into a partial malleable iron structure. The range as specified is found to be suitable.

The silicon content is put just high enough to aid in annealing, i.e., to produce a graphitizing action in the annealing furnace so that the length of time for annealing may be kept economically short. It also plays a part in maintaining fluidity and on casting quality.

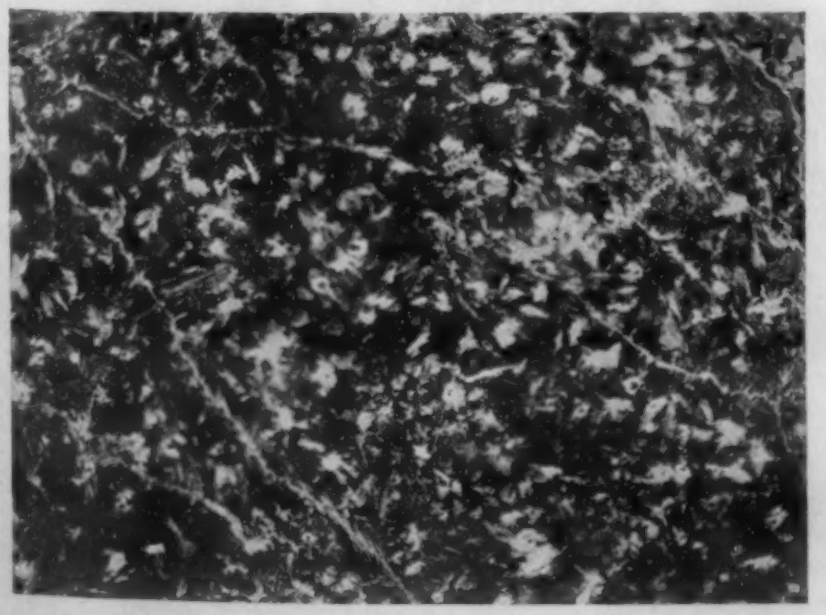
The copper has much the same action as the silicon as far as graphitizing is concerned, but in addition it tends to harden the pearlitic matrix of the final structure. Especially does the copper increase the hardness of some small areas of ferrite that may be present after annealing.

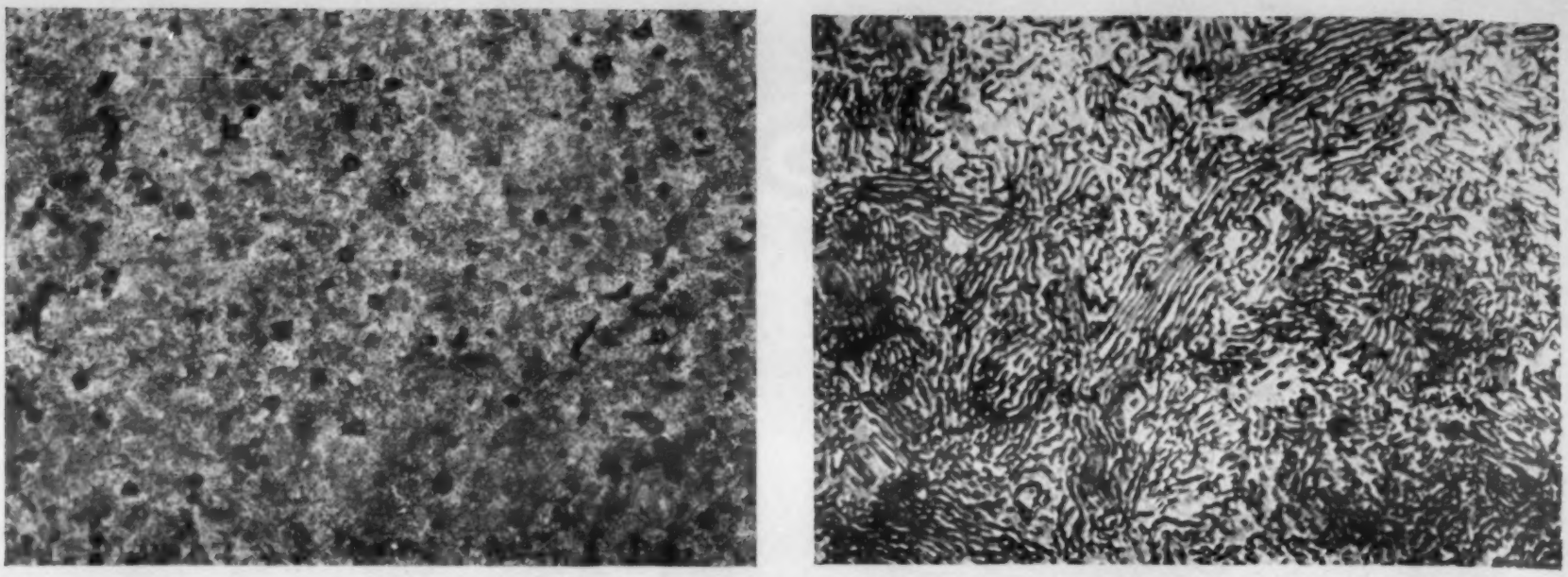
The manganese acts as a matrix hardener and holds enough carbon in solution so that, upon annealing, the desired pearlitic structure is obtained. Ford metallurgists say that a better braking surface could be obtained by increasing the manganese content or by adding some other carbide former but the top limit of the present Brinell hardness of 187 to 241 is about as hard as is now economically machinable.

Brake Drums Made by Other Foundries

These brake drums are not now produced in the Ford foundries but are made by other companies to Ford specifications, both as regards composition and heat treatment. The melting is done in either pulverized-coal-fired Brackels-

Structure of the Alloy in the Brake Drums in the As Cast Condition. Etched in 5 per cent nital. Left is 100 X and right is 1000 X.



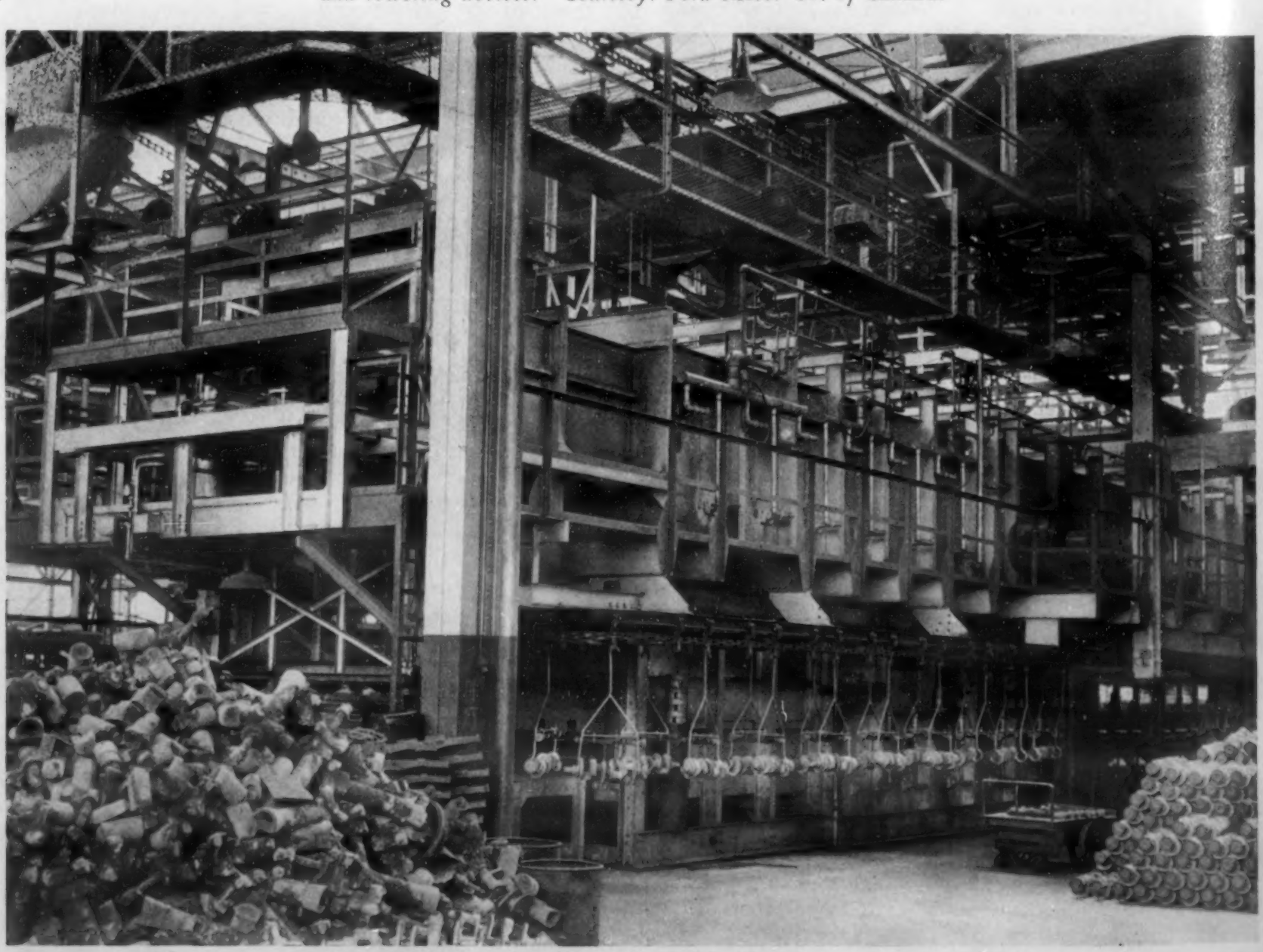


Structure of the Alloy in the Brake Drums after Heat Treatment. Etched in 5 per cent nital. Left is 100 X and right is 1000 X. The latter reveals the lamellar pearlite.

berg furnaces or in electric furnaces. The charge consists generally of return or back scrap, low carbon scrap steel and enough pig iron to insure the correct analysis. The copper is charged as scrap copper with the original charge. The castings are made in green sand, usually two in one mold.

As stated previously the heat treatment is accomplished in two types of gas-fired furnaces. At one of the plants producing these castings a Surface Combustion roller hearth type is used and another company, which produces these castings by electric melting, employs a pusher type Holcroft furnace.

Double Decked Holcroft Heat Treating Furnaces for Copper-Silicon Alloys. The lower furnace handles crankshafts and the upper one wheel hubs or brake drums through a heat treatment cycle of from 6 to 8 hrs. during which a temperature of 1650 deg. F. is reached. Both furnaces are hydraulically operated, the upper one having automatically timed elevating and lowering devices. Courtesy: Ford Motor Co. of Canada.



ATMOSPHERES AND FLUXES IN THE

Melting of Wrought Phosphor Bronze

by L. Kroll, F. E. Ball and E. A. Anderson

Dallas Division, Revere Copper & Brass, Inc., Chicago.

THE LITERATURE IS FULL of contradictions on the proper method of melting phosphor bronze. Some authorities state that oxidizing conditions are very bad, others that oxidizing conditions are necessary. Gas holes, inverse segregation and tin sweat are often linked with the atmosphere under which the metal is melted. Imperfections that affect the mechanical properties, the forming qualities and the ability to take a smooth polish, are likewise ascribed to the conditions of melting.

To throw more light on the effects of variables, a series of heats was made up in a 50-lb. laboratory gas-fired crucible furnace, using clean copper scrap and virgin tin, under various atmospheres. These were cast into chill molds to give flat bars 1¼ in. thick which could be subsequently rolled to sheets for physical properties and Olsen ductility tests. From these heats, samples were also taken for various other tests as described later. The analysis of the heats and the fluxes, covers, or atmospheres used are given in Table I. Save for the exceptions noted in the table, all were poured at 2080 deg. F. Phosphor copper was added at the end of the heat in amount governed by the amount of slag upon, and the appearance of the metal surface, the aim being to have about 0.20 per cent P retained in the metal, save in two cases noted in the table. In one heat sulphur was intentionally added.

It will be seen that with two exceptions, No. 3 and No. 5, the tin content ran between 7.55 and 8.15 per cent. However, the strength in the fully annealed condition was not sensitive to Sn content. No. 10, which was poured at a high temperature, was the strongest and Nos. 8 and 9 the weakest. The two latter were low in P. Fig. 1 shows that the strength is sensitive to the P content. The only heats falling off the curve are No. 10, poured at the high

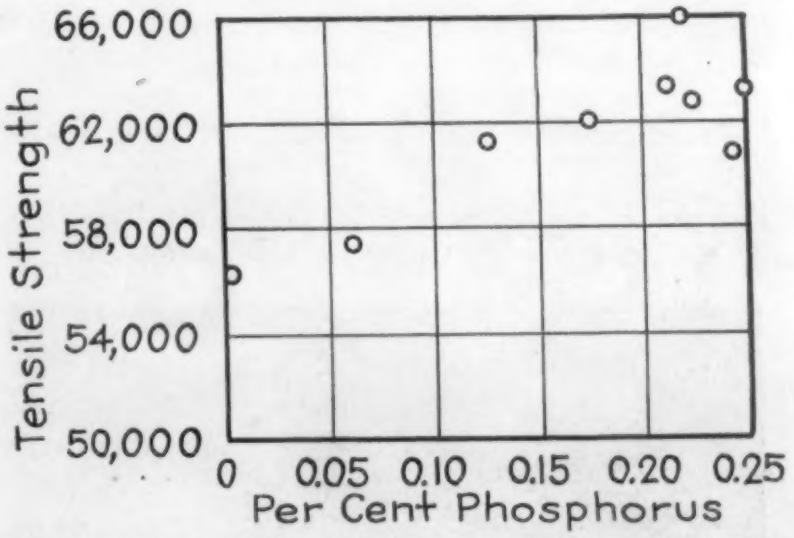


Fig. 1.—Effect of Phosphorus on Tensile Strength of Fully Annealed Bronze Cast under Various Conditions.

Table I—Analyses of the Heats and Fluxes, Covers or Atmospheres Used

Heat No.	Sn per cent	P per cent	Fe per cent	Atmosphere or flux	Special note	Properties of 0.020-in. sheet rolled from flat bars and annealed 45 min. at 1200 deg. F.		
						Tensile strength	Elongation, per cent	Rockwell F
4	8.12	0.180	0.010	Purified N_2		62,000	66.8	89
1	8.00	0.190	0.010	Gas atm.[c], no cover		no test		
2	8.00	0.236	0.003	Charcoal cover		no test		
8	7.72	0.003	0.010	Charcoal cover and glass	No P added	56,100	64.9	88
3	8.53 [a]	0.134	0.010	Dry air, no cover		no test		
11	7.80	0.220	0.014	BaO cover, no charcoal		62,800	63.7	90
7	7.61	0.127	trace	Steam, no charcoal		60,700	66.0	92
5	7.25 [b]	0.218	0.014	Dry H_2, no charcoal		62,400	66.8	91
9	8.04	0.058	trace	Dry H_2, no charcoal	Very low P	57,500	70.7	88
13	7.60	0.250	0.002	C Cl_4, no charcoal		63,200	67.6	89
12	7.90	0.240	0.016	Charcoal—prefrozen [d]		60,900	62.4	89
10	7.58	0.220	0.012	Charcoal and glass	Poured 2300 deg. F.	66,000	64.4	92
6S	7.75	0.206	0.018	Charcoal	0.15 S added	62,900	62.1	93

[a] High Sn. [b] Low Sn. [c] Gas 9.7% CO_2, 1.8% CO, 2.5% H_2, 0.1% O_2; bal., N_2. [d] Allowed to freeze in crucible, immediately remelted.

Fig. 1a.—Fracture of Sample Cast in Iron Mold, Charcoal Cover and Deoxidized with Phosphorus.

temperature and No. 12. This was also on the low side in ductility. No 6S, the sulphurized heat, had normal strength but low ductility.

The properties of sheets from the respective heats which

Fig. 1b.—Fracture of Sample Cast in Iron Mold with Charcoal and Glass Cover, not Deoxidized.

were rolled after annealing for 45 min. at 1100 deg. F. are shown in Table II. After rolling the cast bar by the regular rolling and annealing method to 0.060 in. and annealing at 1100 deg. F., these sheets were rolled to 0.020 in. in thickness or reduced 67 per cent.

No. 8, in Table II to which no P was added, is lowest in strength; No. 10, which was overheated, shows this effect in an extremely high yield and low ductility. Other variations in properties do not stand out enough to allow evalu-

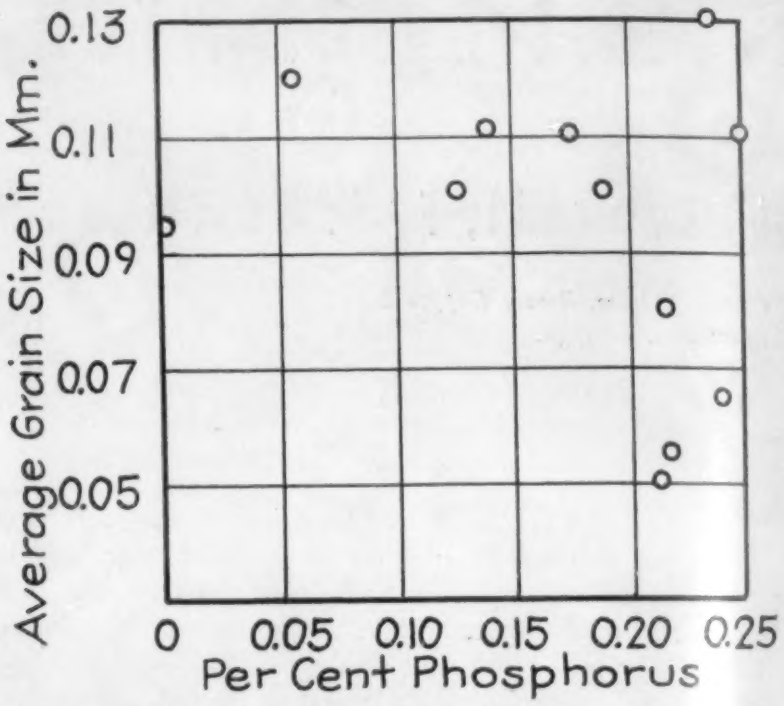


Fig. 2.—Effect of Phosphorus on Grain Size of Bronze Cast under Various Conditions and Annealed at 1400 deg. F.

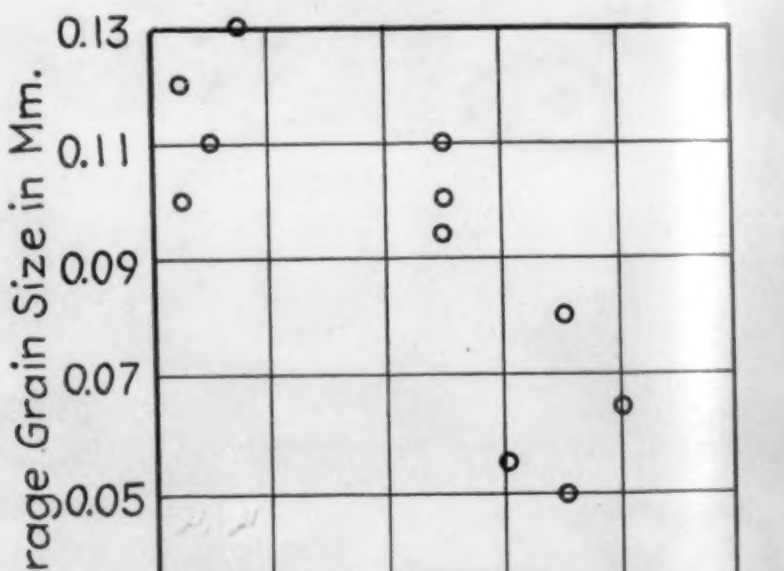


Fig. 2a.—Effect of Iron on Grain Size of Bronze Cast under Various Conditions and Annealed at 1400 deg. F.

Table II—Properties of Sheets Rolled After Annealing at 1100 deg. F.

Heat No.	Tensile, lbs. per sq. in.	Yield, lbs. per sq. in.	Elastic Limit, lbs. per sq. in.	Elongation, per cent	Rockwell B
4	119,600	104,500	82,300	1.60	101
8	114,600	100,500	83,400	1.50	100
11	128,300	112,800	92,400	1.60	103
7	121,000	107,000	90,800	1.50	100
5	124,300	109,700	87,200	1.50	102
9	120,600	110,500	89,500	1.50	102
13	124,500	103,000	91,600	1.50	101
12	126,000	112,300	93,100	1.50	103
10	127,200	125,700	96,400	0.80	102
6S	121,800	109,800	83,200	1.90	102

ation of the melting conditions on the score of mechanical properties. That 6S, with its high S, showed normal mechanical properties, is worthy of note.

The Olsen cupping test for ductility was next examined, with the results given in Table III, after a 1150 deg. F. anneal.

Table III—Olsen Cupping Test for Ductility

Heat No.	Gage	Scleroscope	Olsen value	Grain size, 1150 deg.	Grain size, 1400 deg.
4	0.021	22	0.489	0.11	0.11
1	0.011 [a]	20	0.419 [a]	0.09	0.10
2	0.011 [a]	21	0.420 [a]	0.10	0.13
8	0.021	22	0.492	0.10	0.095
3	0.011 [a]	23	0.428 [a]	0.10	0.11
11	0.021	23	0.490	0.045	0.05
7	0.019	20	0.489	0.095	0.10
5	0.021	25	0.500	0.07	0.08
9	0.020	21	0.490	0.10	0.12
13	0.020	22	0.494	0.12	0.11
12	0.022	23	0.506	0.04	0.065
10	0.021	24	0.506	0.045	0.055
6S	0.019	24	0.430	0.045	0.04

[a] Thin gage.

The Olsen value on the 0.02-in. stock of 0.489 to 0.506 or that of 0.419-0.428 on the 0.01-in. stock, did not vary enough to give any indication of differences in quality. The sulphurized heat, 6S, falls down in Olsen value, as might be expected.

The grain size showed so much variation that it was determined again after a higher anneal, as shown in the last column. Plotting grain size against P gives a shot-gun curve, and there is evidently no relation, but grain size against Fe content (derived from the stirring rod) shows that, when Fe rises above 0.01 per cent, the grain size drops abruptly. (See Fig. 2.) This observation is interesting but needs further checking.

So far all we have learned from the tests cited is that increase in P raises the strength in the fully annealed condition, overheating reduces the ductility in the hard condition, and S injures the Olsen value. No real light has been thrown on the question of the atmosphere, flux or cover in melting. Since the gas content or degree of soundness resulting from the atmosphere used should be reflected by density values, these are compared in Table IV.

Table IV—Density Value Compared

Heat No.	Scoop, 12 hrs., 1200 deg.	Flat bar, 12 hrs., 1200 deg.	Flat bar forged 50 per cent and annealed
4	8.8685	8.8380	8.9238
1	8.8607	8.7839	8.9140
2	8.8478	8.7605	8.9046
8	8.8531	8.5412	8.9261
3	8.8506	8.8393	8.9203
11	8.8511	8.7691	8.9108
7	8.8833	8.8318	8.9263
5	8.8506	8.7701	8.9165
9	8.8901	8.8206	8.9364
13	8.8407	8.7511	8.9117
12	8.8612	8.8219	8.9131
10	8.8244	8.7053	8.9018
6S	8.8239	8.7498	8.8398

The *scoop sample,* previously described, METALS AND ALLOYS, Oct. 1936, p. 261, Jan. 1937, p. 25 is designed to eliminate variables that may enter in pouring. The rapid chilling of this prevents the evolution of gas that will occur in slower freezing, so that the behavior of the flat bars, whose rate of freezing is more like that of the commercial product, is probably a more sensitive indicator of gasiness. Any of the density specimens, however, will pick out the fact that the overheated Lot. No. 10 is in a class by itself as to low density.

From the others, Nos. 9, 7, 8, 4 and 3 stand out in the forged and annealed condition, and in most cases they are also among the denser specimens in the unforged condition and in the scoop sample. In spite of the idea that hydrogen or water vapor causes gasiness, Nos. 9 and 7, in hydrogen and steam, have not given low density. It will also be noted that, though P is necessary to control gas, Nos. 9 and 3 with no, or very little, P are well up in density. No. 5, in hydrogen with P added has one of the lowest densities. No. 3 in air, without any charcoal cover or other protection, is by no means the worst of the lot as to density.

Fig. 3.—Structure of Alloy No. 4 Melted under Nitrogen. Cleanest of all. Magnification 75X.

Fig. 4.—Structure of Alloy No. 13 Melted under CCl_4. Very clean. Magnification 75X.

Fig. 5.—Structure of Alloy No. 11 Melted under BaO. Very clean and fine grained. Magnification 75X.

The picture painted by the density figures is not very clear and other methods of differentiation must be sought.

Turning to the question of tin sweat and inverse segregation, tin sweat occurred in No. 9, a low P heat (but did not appear in No. 8 without P) and in the overheated No. 10. Analyses for Cu of round bar castings made in an iron mold on samples near the surface and halfway from surface to center gave the results in Table V.

Table V—Analyses for Copper

Heat No.	Surface	Halfway in	Difference
4	91.49	91.87	0.38
2	91.82	91.98	0.16
8	91.66	92.13	0.47
3	93.12	93.47	0.35
11	91.62	91.96	0.34
7	91.50	91.91	0.41
5	91.81	92.38	0.57
9	91.54	92.11	0.57
13	91.44	91.79	0.35
12	91.71	91.86	0.15
10	91.49	91.76	0.25
6S	91.14	91.57	0.43

Nos. 2 and 12 with charcoal showed the least difference, while Nos. 5 and 9 under hydrogen, showed the most. Distinctions again are not clear cut. Visual examination of fractures was made on bars cast in a variety of ways as revealed in Table VI.

Table VI—Visual Examination of Fractures

Heat No.	Scoop	Round bar in iron mold	Round bar in sand mold
4	No trace of gas	Trace	Trace
1	No trace of gas	.....	.....
2	No trace of gas	Trace	Very spongy
8	No trace of gas	Much gas	Much gas
3	No trace of gas	No trace	No trace
11	No trace of gas	No trace	No trace
7	No trace of gas	No trace	No trace
5	No trace of gas	Trace	Spongy
9	No trace of gas	Very much gas	Very much gas
13	No trace of gas	Trace	Trace
12	Some gas	Trace	Trace
10	No trace of gas	None	None
6S	No trace of gas	None	None

Although the overheated Lot 10 had low density, it showed no gas to the naked eye. (We shall later see that on microscopic examination of the slow cooled bar it did show gas) Nos. 2, 8, 5 and 9 all showed up poorly in the slowly cooled bars. These had, respectively, charcoal cover, with P; charcoal cover, no P; hydrogen atmosphere with P; hydrogen atmosphere with low P. The difference between P and no P is shown in Fig. 1 in which the slowly cooled bar fractures of Lot 2 and Lot 8 are compared. Nos. 3, 11 and 7 come through this examination with no trace of gas. These were melted, respectively, in air without protection, under BaO without charcoal, and in steam without charcoal.

Results of examining the fractures under 50 dia. magnification, are listed in Table VII:

Fig. 6.—Structure of Alloy No. 2 Melted under Charcoal Cover and Normal Practice. Magnification 75X.

Table VII—Fracture Examination at 50x

Heat No.	Scoop	Round bar in chill	Round bar in sand
4	No trace	Trace	Trace
1	Trace	.....	.....
2	No trace	Gassed	Spongy and gassed; gray spots
8	Trace	Much gas	Much gas
3	No trace	No trace	Gassed
11	No trace	Trace	No trace; gray spots
7	No trace	Trace	Gassed gray spots
5	No trace	Gassed	Spongy but not gassed
9	Lightly gassed	Much gas	Much gas
13	No trace	Trace	Trace; gray spots
12	Trace	Trace	Trace; gray spots
10	No trace	Gassed	Much gas; gray spots
6S	No trace	No trace	No trace

Leaving out 6S, those that lead in freedom from gas or sponginess are Nos. 11, 7, 4, 13 and 12, respectively under BaO, steam, nitrogen, CCl_4, and under charcoal with freezing and remelting.

Examination, by eye, of the fracture of flat bars from which sheet was rolled gave the results in Table VIII.

Fig. 7.—Structure of Alloy No 8 Melted under Charcoal and Glass with no Phosphorus. Dirty. Magnification 75X.

Table VIII—Fracture Examination by the Eye

No.	Gas	No.	Gas
4	Trace	7	Trace
1	.....	5	Trace
2	Trace	9	Little
8	Much gas	13	None
3	None	12	None
		10	None
11	Trace	6S	None

Fig. 9.—Structure of Alloy No. 3 Melted in Air with No Cover. Quite clean. Magnification 75X.

Fig. 8.—Structure of Alloy No. 5 Melted under Hydrogen. Very clean. Magnification 75X.

Examination, by eye of the surfaces of the annealed sheet from the flat bars showed Nos. 9 and 10 defective; the others showed no surface defects.

The annealed sheet rolled from the flat bars was given a microscopic examination and count of defects and inclusions at 150 dia. The results are given in Table IX.

Fig 10.—Structure of Alloy No. 10 Melted under Charcoal and Glass. Overheated and dirty. Magnification 75X.

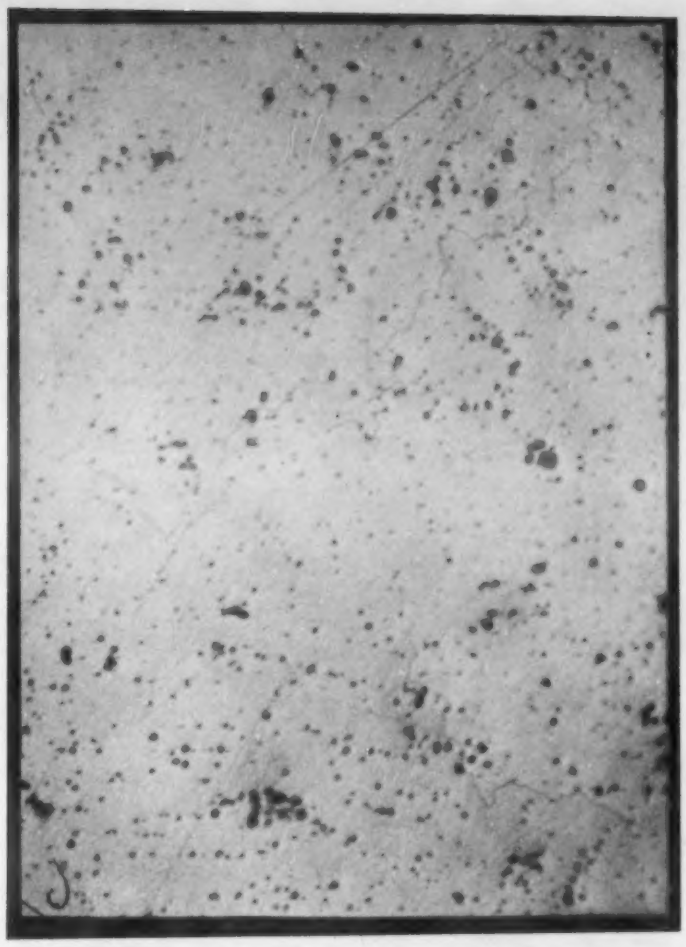


Fig. 11.—Structure of Alloy No. 6 Unetched and Sulphurized from Scoop Sample. Magnification 75X.

Table IX—Microscopic Examination at 150x of Annealed Sheets

No.	Melting	No. of defects in 10 sq. in.	
4	Nitrogen	14	Surface appearance very good
1	Gas (see footnote Table I)	174	Fair
2	Charcoal	243	Fair
8	Charcoal and glass, no P	290	Bad, one large defect
3	No cover, air	155	Fair, one rather large defect
11	BaO, no charcoal	100	Good surface appearance
7	Steam, no charcoal	293	Fair
5	H_2, no charcoal	127	Good surface appearance
9	H_2, no charcoal, low P	454	Surface appearance very bad
13	CCl_4, no charcoal	60	Surface appearance very good
12	Charcoal, frozen and remelted	330	Good surface appearance
10	Charcoal and glass—high temp.	200	Worst surface appearance *
6S	Charcoal (S added)	Full of inclusions.	Bad

* Most defects small, but one very large group of defects.
Micrographs at 75X in Figs. 3-11 illustrate the appearance of some of the heats.

From the point of view of cleanliness the heats melted without access of air or of hydrogen, CO_2, steam, etc. (that is, those under N_2 and CCl_4) showed up the best. The BaO flux was also quite promising.

The presence of a reasonable amount of P and the avoidance of overheating (at least on metal under the usual charcoal cover) were definitely indicated as necessary.

The relatively fair behavior of metal melted under hydrogen and properly phosphorized was of interest in view of the many comments on the hazard of gasiness in presence of hydrogen. The soundness of the heat to which S was added was also surprising.

The laboratory tests were supplemented by two induction furnace heats in the shop, one to duplicate No. 3, i.e., in air without charcoal or other cover, the other under hydrogen, to duplicate No. 5. The former showed only traces of gas on examination of the fracture, the latter showed a trifle more but when the sheet from each was rolled to finish gage the surface appearance was similar, and could not be differentiated from that of the usual commercial melts under charcoal.

It would appear that, in phosphor bronze, neither an oxidizing nor a reducing atmosphere is fatal in melting; the use of sufficient P and the avoidance of overheating seem to be more vital precautions.

Our own appraisal of the quality of the experimental melts, on the basis of all the data, for properly phosphorized heats, not overheated, puts them in the following order from best to worst:

	No.	Melted under
A:	4	Nitrogen
	13	CCl_4
B:	12	Charcoal, frozen and remelted
	11	BaO
C:	3	Air—no cover
	1	Gas
	2	Charcoal
	5	Hydrogen
	7	Steam

The non-phosphorized or too-lightly phosphorized heats No. 8 and 9, the overheated melt No. 10, and the sulphurized heat 6S all had very obvious faults which put them in a different category from the rest.

While neither melting in air without charcoal nor under hydrogen gives results superior to the usual practice of melting under charcoal, such practice was not found as harmful as the literature would indicate.

On the other hand, exclusion of air and reducing gas by use of gas inert to the melt, nitrogen or carbon tetrachloride did show advantages, though the inert gas method would not be commercially convenient. The cleanness of the melt made under BaO indicates that this cover deserves further attention.

A CORRELATED ABSTRACT ON

Corrosion and Corrosion-Resistant METALS AND ALLOYS

by V. V. Kendall

Section Editor, Current Metallurgical Abstracts of METALS AND ALLOYS

DURING THE LAST FEW YEARS, augmented interest in corrosion and corrosion-resistant metals and alloys has been shown by the increased number of papers in various society and metallurgical publications culminating in a series of symposia during 1936 which comprised a total of some 48 papers on the physical properties, applications, and corrosion resistance of metals and alloys. These symposia were: In England, the Chemical Engineering Congress of the World Power Conference; and in the United States, the American Society for Testing Materials' "Symposium on High-Strength Constructional Metals," the American Chemical Society's "Symposium on New Metals and Alloys Applicable to the Chemical Industry," the American Society of Civil Engineers' symposium on "Structural Applications of Steel and Light-Weight Alloys" and the American Society of Mechanical Engineers' "Symposium on Corrosion-Resistant Metals in Design of Machinery and Equipment."

The viewpoints and the memberships of these societies vary, with the result that duplication in the field covered or the data presented at the time of the symposium is of little moment. However, when all the papers are pub-

Lemon Juice Extractor Fabricated Completely from 18-8 Stainless Steel. Reaming burrs, flush guards, collecting ring, and gathering tube included. Even the motor shafts are made from free machining stainless steel.

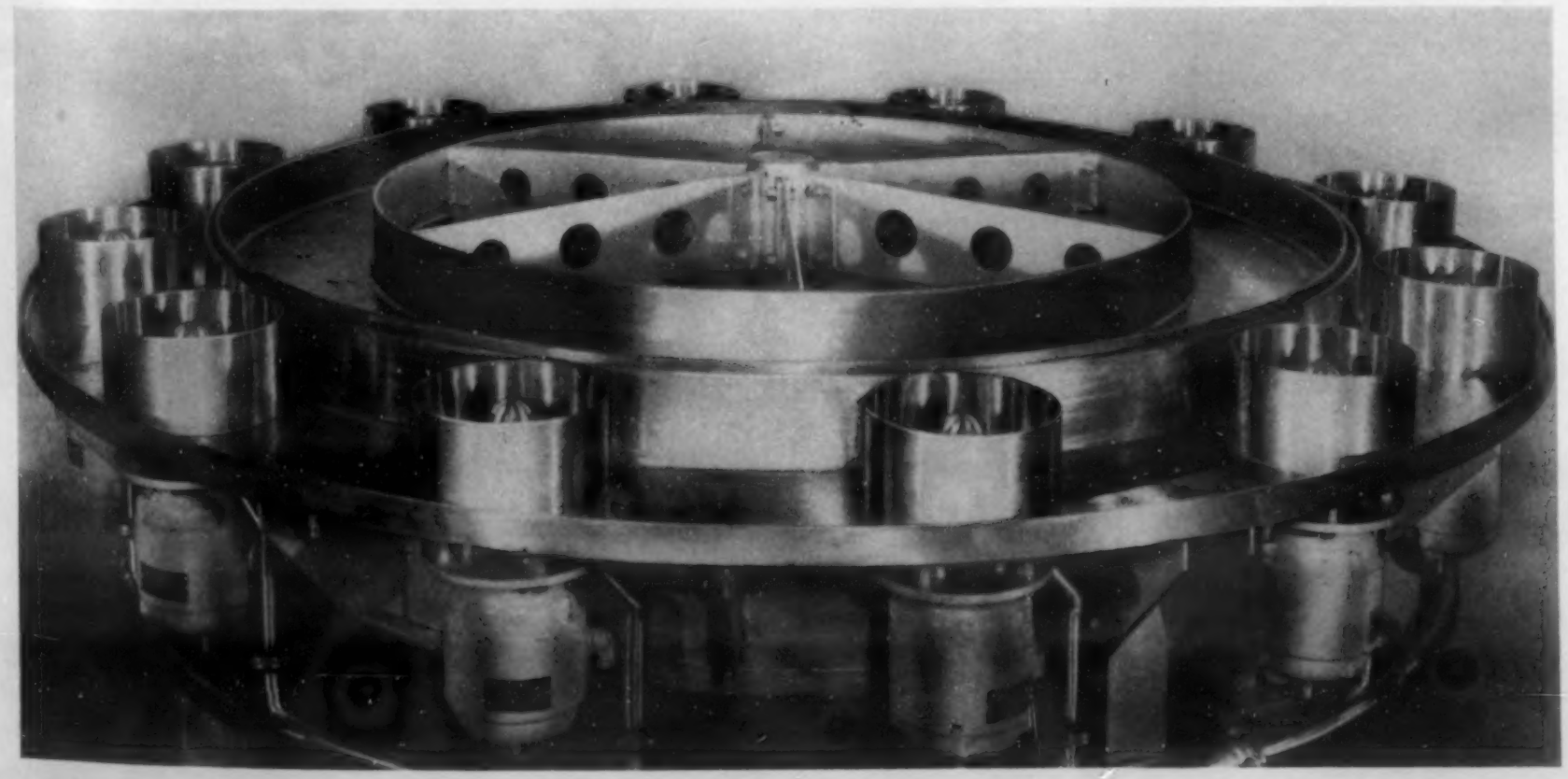


TABLE I—Chemical and Physical Qualities of Chromium and Chromium-Nickel Alloys

Item No.	Alloy No.[f]	Chemical Analysis (Percentages) Carbon[a] (1)	Chromium From: (2)	Chromium To: (3)	Nickel From: (4)	Nickel To: (5)	Silicon[b] From: (6)	Silicon[b] To: (7)	Other Elements From: (8)	Other Elements To: (9)	Physical Properties Yield Point Stress in Kips per Sq. In. From: (10)	Yield Point Stress in Kips per Sq. In. To: (11)
1[g]	12 Cr	0.12	12.0	14.0	...	...	...	...	...	...	40	170
2[g]	12 Cr	0.12	12.0	15.0	...	...	(0.20)[j]	(0.40)[j]	0.45[l]	0.65[l]	40	150
3[h]	18 Cr	0.12	16.0	18.0	...	...	...	...	...	...	40	100
4[i]	28 Cr	0.20	23.0	30.0	...	...	...	...	...	...	..	45
5[h]	18-8	0.20	17.0	19.0	7.0	9.5	...	...	...	...	35	225
6[h]	18-8	0.20	17.0	19.0	7.0	9.5	...	...	0.15[m]	0.30[m]	45	130
7[i]	18-8	0.20	17.0	19.0	7.0	9.5	2.0	3.0	...	...	..	40
8	18-8	0.11	16.0	19.0	9.0	14.0	...	...	2.0[l]	4.0[l]	40	130
9[h]	18-8	0.11	17.0	19.0	7.0	10.0	...	...	(4)[r]	(4)[n]	35	200
10[h]	18-8	0.15	17.0	19.0	8.0	12.0	...	...	(6)[r]	(10)[o]	40	200
11[i]	25-12	0.20	22.0	26.0	11.0	14.0	...	2.0[k]	...	...	..	40
12[i]	25-20	0.25	24.0	26.0	19.0	21.0	...	..[k]	...	...	..	40

Item No.	Physical Properties (Cont.) Tensile Strength, in Kips per Sq. In. From:[e] (12)	Tensile Strength, in Kips per Sq. In. To:[d] (13)	Elongation in 2 In. Per cent From:[e] (14)	Elongation in 2 In. Per cent To:[d] (15)	Reduction in Area Per cent From:[e] (16)	Reduction in Area Per cent To:[d] (17)	Creep Strength for 1% Elongation per 10,000 Hrs., in Kips per Sq. In. at deg. C. 900 (18)	1,000 (19)	1,100 (20)	1,200 (21)	1,300 (22)	1,400 (23)	1,500 (24)	Modulus of elasticity, in lbs. per sq. in. (25)
1[g]	70	200	28	10	65	25	..	12	5.0	2.2	1.6	1.1	0.7	28,000,000
2[g]	70	175	25	10	60	30	..	..	..	..	..	..	..	28,000,000
3[h]	70	125	28	10	60	25	..	9	5.3	2.0	1.4	1.0	0.6	29,000,000
4[i]	..	75	28	..	60	..	..	..	3.5	1.7	0.8	0.2	..	29,000,000
5[h]	85	275	55	6	65	30	24	18	11.0	7.0	4.5	2.6	0.9	29,000,000
6[h]	100	160	55	20	60	40	..	..	..	..	..	..	..	29,000,000
7[i]	..	90	50	..	60	..	..	19	12.0	7.0	4.6	2.5	..	29,000,000
8	90	160	55	20	65	50	..	..	..	..	..	..	..	29,000,000
9[h]	85	250	55	5	65	30	..	..	14.0	8.0	6.0	3.0	..	29,000,000
10[h]	85	225	55	5	65	30	..	..	..	..	..	..	..	29,000,000
11[i]	..	90	55	..	65	..	..	..	..	..	..	..	..	29,000,000
12[i]	..	90	50	..	55	..	..	21	13.0	7.5	0.5	2.8	..	29,000,000

Item No.	Coefficient of Expansion at A, deg. C. Values of A From 0 deg. to: (26)	Coefficient, $\times 10^{-6}$ (27)	Magnetic properties (28)	Welding properties (29)	Heat treatment properties (30)	Heat conditions,[c] in calories per cu. cm. per deg. C. (31)	Scaling Temperatures, in Deg. Continuous (32)	Scaling Temperatures, in Deg. Intermittent (33)	Brinell Hardness No. From:[e] (34)	Brinell Hardness No. To:[d] (35)	Izod Impact, in Ft. Lbs. From:[e] (36)	Izod Impact, in Ft. Lbs. To:[d] (37)
1[g]	800	12.6	Yes	Poor[p]	Good	0.05	1,400	1,400	160	418	100	30
2[g]	800	12.6	Yes	Poor[p]	Fair[r]	0.05	1,400	1,400	160	340	70	20
3[h]	800	11.2	Yes	Poor[p]	None	0.045	1,500	1,600	160	255	70	1
4[i]	1,000	13.0	Yes	Poor[p]	None	0.04	2,000	2,100	160	...	30	1
5[h]	800	20.0	No	Good	None	0.035	1,600	1,400	156	418	110	10
6[h]	800	20.0	No	Fair[q]	None	0.035	1,400	1,400	179	350	80	10
7[i]	800	20.0	No	Good	None	0.035	1,700	1,500	156	...	80	..
8	800	20.0	No	Good	None	0.035	....	....	160	350	110	50
9[h]	800	20.0	No	Good	None	0.035	1,600	1,400	156	396	100	10
10[h]	800	20.0	No	Good	None	0.035	1,600	1,400	160	350	90	15
11[i]	1,000	20.2	No	Good	None	0.03	2,000	1,600	160	...	90	..
12[i]	1,000	22.5	No	Good	None	0.03	2,050	1,700	160	...	90	..

[a] Maximum allowable. [b] Except Item No. 2. [c] Annealed. [d] Heat-treated or cold-drawn. [e] Soft steel, 0.10 calories per cu. cm. per deg. C. [f] Trade designation by which the alloy is commonly recognized. [g] Heat-treated to improve physical properties. [h] Cold-worked to improve physical properties. [i] These items will harden on cold-working but since they are used only for heat resistance they are annealed only. [j] Sulphur. [k] Maximum. [l] Molybdenum. [m] Selenium. [n] Titanium four times the carbon content. [o] Columbium six to ten times the carbon content. [p] Brittle welds. [q] May check. [r] Fair to good. 1 kip = 1,000 lb.

lished, duplication is necessarily present and the reader is appalled at the amount of reading involved if he were to obtain all the information presented in the field in which he is interested.

It was considered that a correlated abstract of these papers would serve a useful purpose both in collecting the more recent data and in assisting the reader to choose papers of particular interest for more careful perusal.

During the last few decades structural engineering design has become very much standardized. Its theory is based upon idealized materials which assume perfectly elastic properties of the materials. Such phenomena as stress concentration, fatigue and creep have been neglected. A comprehensive review of newer design theory and methods of attack, outlining broadly the factors to be considered is given by Karpov[1], Templin[2] and Brahtz.[3]

High Strength and Light Structural Steels

The low-alloyed structural steels have been used for many years but the increased demands and increased size of structures has necessitated the development of higher strength and lighter steels. The evolution of high-strength structural steels is traced by Moisseiff[25] and the application of alloy steels to light weight construction by Ragsdale.[26] The low-alloy structural steels are also reviewed by Bain and Llewellyn[21] from the standpoint of the effect of the various elements on physical properties. Actual applications of such steels in bridges and buildings are described by Beard.[24]

The stainless high-alloy structural steels are being extensively used in the structural engineering field as reported by Morris.[22] Examples of applications are given which include dam construction, where they are used for gate-rollers, guides, seal strip and screw mechanism for raising and lowering the gates; sewage disposal plants, intakes, reinforced concrete and irrigation. Table I (from Morris) gives the range of physical properties of the most common high-alloy steels.

While physical properties are generally of paramount importance in the design of any structure whether intended for roofing, bridges, chemical plant, oil refining, transportation of oil, gas or water, yet the maintenance of the original properties of the material is of even greater importance. Our recognition of this fact is evident in the safety factor used in every structure in which metallic materials are used. This safety factor attempts to allow for the variation of

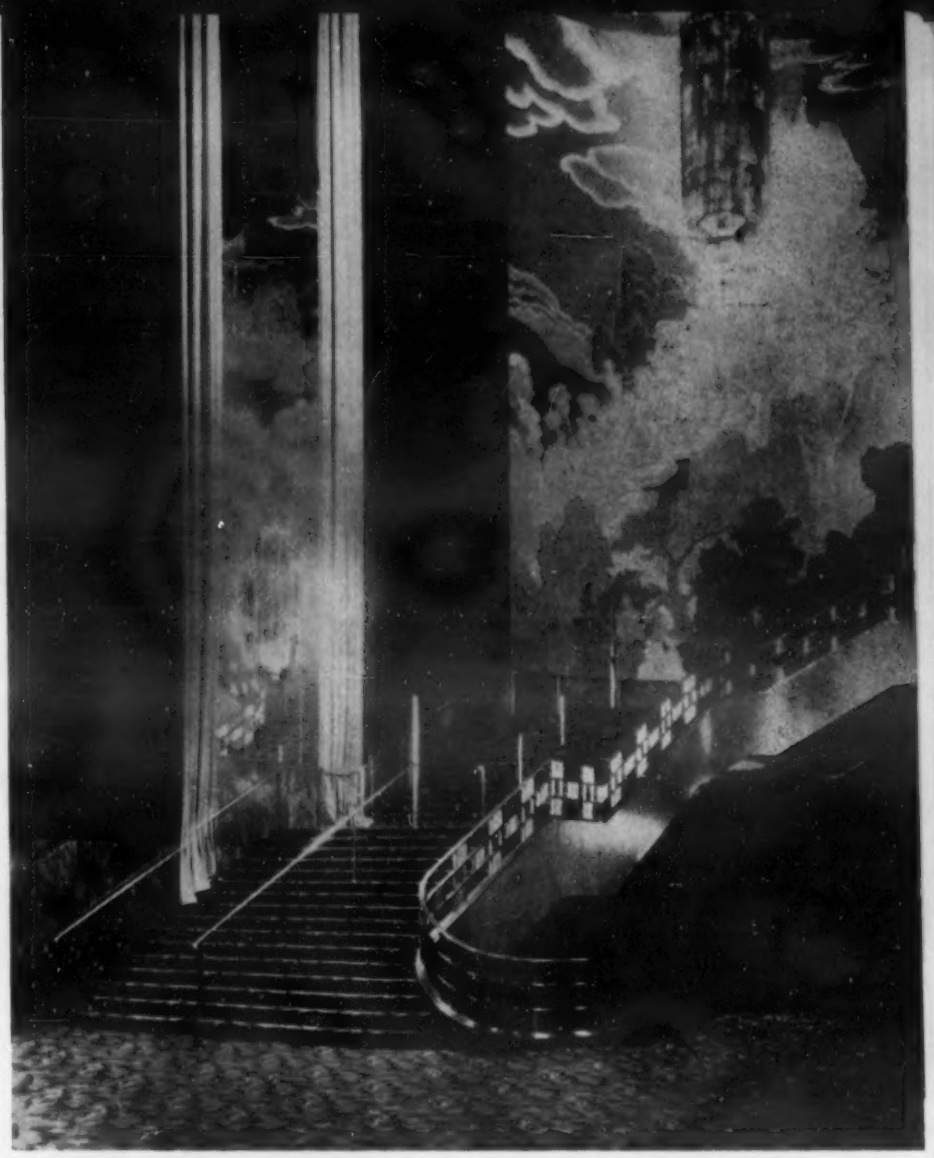
physical properties due to their normal variation in the routine manufacturing process and also for the deterioration of metallic equipment due to service conditions. In some cases the resistance to corrosion is the important factor. In any case it must be considered.

Physical properties are easily determined, if we ignore certain controversies on short time tests, etc. The determination of what a material will do, however, under conditions of service, whether mild or severe, is far more difficult. This is attested by the many criticisms of the present accelerated methods of corrosion testing. The present status of corrosion testing will be discussed in a summary of the Symposium on Corrosion Testing by the American Society for Testing Materials in a later section of this review. Four papers dealing especially with corrosion are listed, those by Fenwick and Johnston[17], Speller[27] and Aston[23] covering theory, factors and experiences and the other by Kühr and Pfeiffer[9] who describe the sulphate reduction process, particularly applicable to soils in The Netherlands, and also the requirements of coal tar and asphalt coatings for pipe.

Chromium the Base of Corrosion-Resistant Steels

The basis of modern corrosion-resistant steels is chromium. Other elements when added to chromium add their peculiarities to the resultant alloys but the fact remains that chromium is the starting point from which corrosion-resistant alloys are built up. The effect of increasing chromium is not linear. Under air oxidation conditions at, say, 1000 deg. C. there is a sharp break in the curve at 4-6 per cent Cr and again at 18-20 per cent Cr while under conditions of corrosive crude oils at high temperature and pressure, there is a sharp decrease in corrosive attack up to 2 per cent Cr after which the decrease is linear but slower.

The quality of stainlessness, which is "stainless" only as regards certain media, does not develop until the range of 12 to 14 per cent Cr is reached. The resistance of chromium steels is considered to be due to the character of the very thin oxide film existent on the surface of the metal. Even small percentages of chromium or of certain other elements such as copper modify the voluminous, loosely adherent rust coating formed on mild steel to a dense, tightly adherent rust coating that is definitely protective.



The Grand Staircase in Radio City Music Hall. An excellent excellent example of permanence, beauty and dignity achieved through stainless trimming.

Amphibian Airplane "Sea Bird" Built by Fleetwings, Inc. Stainless Steel Used for Practically Every Part Except Motor and Wing Covers. Notice the exceptionally smooth, neat, rivetless construction made possible by the "shotweld" process.

The combination of other elements contributes to this effect and thus, industrially, we have a large number of low-alloyed steels on the market which contain various combinations of small amounts of chromium, nickel, silicon, manganese, vanadium, molybdenum and phosphorus, which offer certain advantages of improved physical properties and greater corrosion resistance over ordinary mild or structural carbon steel. These steels generally contain less than 2 per cent Cr or of other individual alloying elements. They were reviewed in the March, 1936, issue of METALS AND ALLOYS. Some additional data on such steels may be added.

Use of Other Metals

Beneficial results may be obtained by the use of other metals besides chromium. Pilling[14a] reports the data in Table II from a 11-year test on nickel-copper steel sheets exposed to various types of atmospheres.

Table II—Atmospheric Corrosion of 0.020 in. Thick Strip

Type	Composition			Life to first perforation in years			
	C	Cu	Ni	Rural	Marine	Moderate Industrial	Heavy Industrial
Ingot iron.....	0.04	...	...	over 10	1.5	1.5	1.5
Copper steel...	0.07	0.17	...	over 10	1.5	3.0	2.1
2% Ni-Cu steel	0.07	0.01	1.39	over 10	over 5	4.0	3.2
4% Ni-Cu steel	0.11	1.18	2.76	over 10	over 5	6.0	10.0
6% Ni-Cu steel	0.08	1.8	4.2	over 10	5	8.0	over 10

Notable progress has been made in the development of two types of heat-treated, low-carbon, nickel-molybdenum steels for oil well sucker rods, containing (1) 0.20 per cent C, 1.75 per cent Ni and 0.25 per cent Mo and (2) 0.05 per cent C, 3.50 per cent Ni and 0.25 per cent Mo. These steels exhibit a much lower susceptibility to sulphide embrittlement and a high comparative resistance to corrosion and sulphide corrosion fatigue.[17b]

For high-pressure service, where resistance to shock and the decarburizing effect of hydrogen at high temperatures is required, good results are obtained with 1.50 to 2.75 per cent Cr and the addition of Mo and V.[18] The addition of 0.5 to 1 per cent each of Mo and Si to this chromium is used for higher high-temperature strength and better resistance to oxidation.[18c]

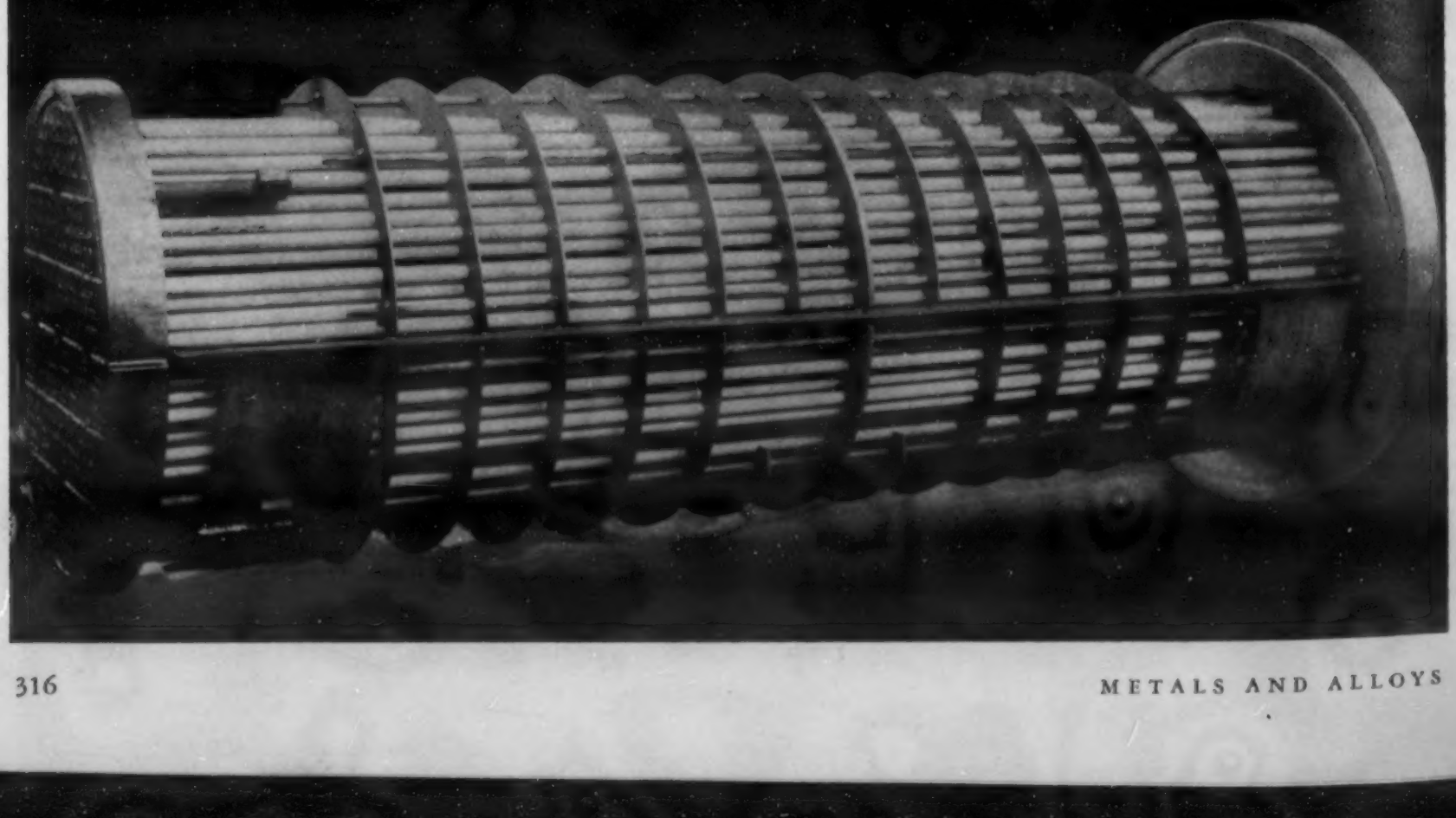
The 4 to 6 per cent Cr steel with its properties modified by other elements, particularly 0.5 per cent Mo, has now become firmly established for use in ammonia plants, high-pressure steam service and in oil refining where it is used for oil still tubes, return bends, oil pump impellers, flow line headers, pipe fittings, and valve trim. The 4 to 6 per cent Cr steel is subject to air-hardening thus handicapping its use for welding and fabricating. Air-hardening has been almost entirely eliminated by the addition of columbium or titanium [18c] or the addition of 1 per cent aluminum.[17b] A steel containing 8 to 10 per cent Cr with Mo has been recently introduced. It has better creep strength and non-scaling properties up to 1200 deg. F. and is reported to be better than 4 to 6 per cent Cr steel for hot oils and vapors.[18] Another substitute for 4 to 6 per cent Cr steel where conditions are less severe with also less cost is a 3 per cent Cr—0.5 per cent Mo steel recently developed.[17b]

A special group of steels containing approximately 8 per cent Cr with several per cent of silicon, with or without aluminum, has found wide use as valve steels against combustion gases.[29] They are also used in automotive and airplane engines.

The Plain Chromium Steels

The 11.5 to 14 per cent Cr group contains the original "stainless" steel which contained 13 per cent Cr and about 0.30 per cent C and required hardening and polishing. With carbon under 0.12 per cent this steel has a wide range of physical properties which can be obtained by simple heat treatment. It is used for steam and hydraulic turbine blades because of its high resistance to erosion and cavitation. It is also used in the form of tubes, valves and fittings for high-pressure steam service. The addition of 2 to 3 per cent W to this steel raises the temperature at which the alloy loses its temper from 750 to 900 deg. F. At 1050 deg. F. the creep strength is increased over four

Heat Exchanger Constructed of Stainless Tubes for Special Corrosive Service. Stainless and heat-resisting seamless tubes are the ideal choice for all tubular heat transfer equipment.



times Resistance to oxidation is increased. Up to 1500 deg. F it was twice as good as the regular 18 and 8.[18a]

The 16 to 20 per cent Cr steel (0.12 per cent C max.) possesses increased corrosion and oxidation resistance with improved physical properties. It is fully resistant to nitric acid, and large tonnages have been used for such equipment as absorption towers, tanks, piping, fittings, heat exchangers, and retorts employed in the ammonia oxidation process. It is extensively used in the chemical industry. Its ductility after rolling can be increased by the addition of columbium and titanium. The addition of nitrogen produces a finer grained structure and retards grain growth at elevated temperatures, without detracting from its resistance to chemical corrosion. The addition of 1 or 2 per cent Ni hardens and raises the strength of this steel when heat treated, making it suitable for aircraft construction. Resistance to salt water and non-oxidizing acids, such as hydrochloric, is improved by the addition of silicon and copper.[18] It is used in the paper industry to resist the action of alum and sulphite liquors and for equipment in the food industry where corrosion is less severe but where cleanliness and freedom from metallic contamination are most important.

The 25 per cent Cr steels not only have improved general corrosion resistance but also are exceedingly resistant to oxidation at elevated temperatures. They are used in the handling of superheated steam and food products, and, in particular, as furnace muffles, annealing boxes, and similar applications where temperatures are lower than about 900 deg C. The addition of nitrogen, especially in the presence of a small amount of nickel, to this analysis definitely refines the grain, improves its shock resistance, and materially reduces the rate of grain growth at high temperature.[29] An alloy containing 28 per cent Cr with over 1 per cent Si has been found to be very good for the manufacture of high-purity phosphoric acid.[18] A new alloy containing 35 per cent Cr and 7 per cent Al has been developed which is good for continuous service at 2300 deg. F.[18]

The Austenitic Group

Above the plain chromium steels is the austenitic group, the most popular member of which is the 18 and 8 Cr-Ni alloy. These steels have great general corrosion resistance and remarkable physical properties. They are readily rolled, fabricate without difficulty and, with columbium or titanium present, offer no difficulties in welding. Manganese has been used to replace the nickel in the 18 and 8 composition. Where sulphurous gases are involved or where hydrogen sulphide or similar reducing acids are present in solution, manganese affords greater protection than nickel. On the other hand where chlorides and certain organic acids must be resisted, nickel confers properties superior to those conferred by the manganese.[29]

Various combinations of chromium and nickel are used in the higher alloyed materials. Such analyses as 25-12, 25-20, 30-25, 25-15, 35-18, also modified by the addition of other metals are used for special purposes.

Alloys for Sulphite Pulp Industry

The 20-10 Cr-Ni alloy has been found to be an excellent alloy for the sulphite pulp industry. Under these conditions its corrosion rate is only about one-sixth that of the regular 18 and 8 steel and approximately one-half that of the 18 and 8 steel containing 2 per cent Mo. In this application cellulose products are being made which are practically free from metallic contamination.[18a]

Tanks for Processing a Highly Corrosive Embalming Agent Containing Dissolved Gas under Pressure, Built Throughout of 18-8 Stainless.

> In the pulp and paper industry, Miller [20] also reports as follows. "At present the most serviceable and popular alloys for castings are those containing about 28 per cent Cr and 10 per cent Ni plus (in some cases) 3 per cent Mo, and those containing about 20 per cent Cr, 10 per cent Ni, and 3 per cent Mo. In the wrought form the best all-round material is the alloy containing approximately 18 per cent Cr, 8 per cent Ni, and 3 per cent Mo, although an alloy containing about 27 per cent Cr, 4.5 per cent Ni, and 1.5 per cent Mo is coming into use, especially for piping, because of the difficulty of obtaining seamless tubes of the former alloy. Cast pipe in long lengths of various compositions is being produced by the flash butt welding of centrifugally cast tubes."

The 12.5-12.5 Cr-Ni steel provides superior corrosion resistance to the plain chromium steels together with great ductility, rendering it particularly suitable for cold working operations such as deep pressing.[5]

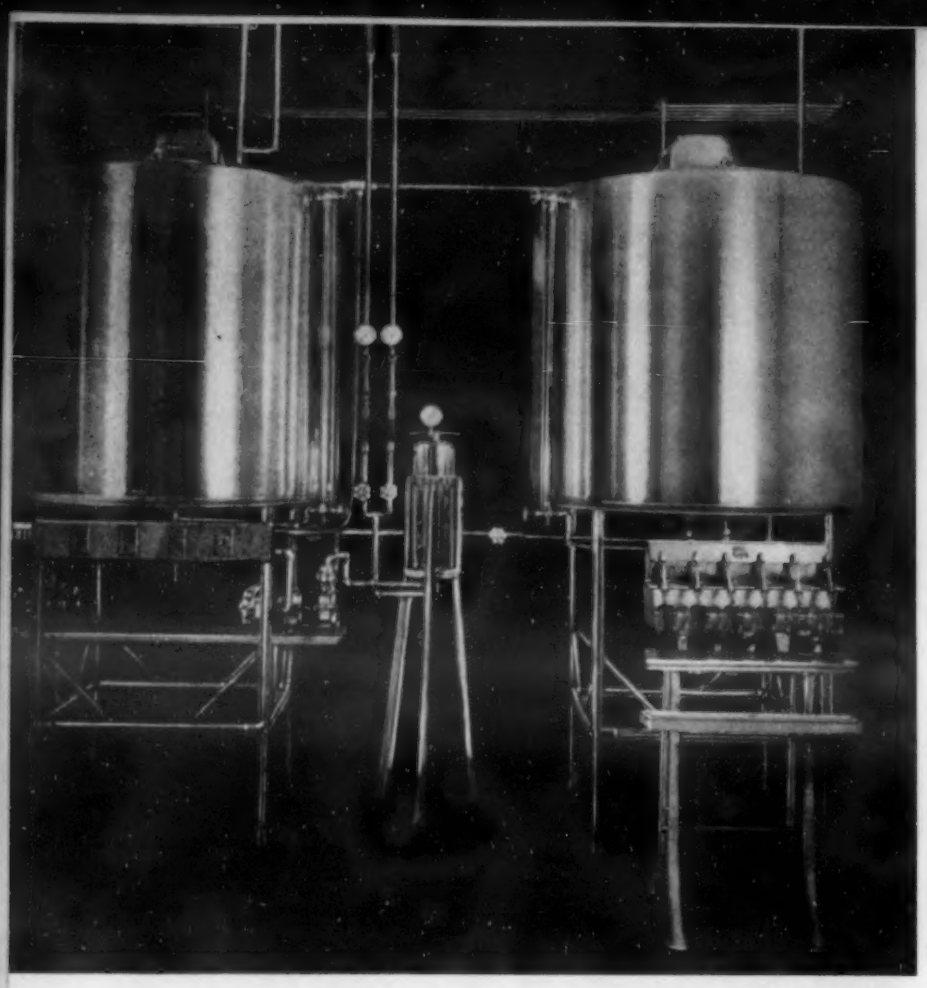
The addition of Mo to 18 and 8 confers special acid-resisting properties, e.g., to acetic and sulphuric acids.[5]

The 20-9-1.3 Cr-Ni-Ti steel was made to provide a material having a corrosion resistance comparable with that of the ordinary 18 and 8 steels but having in addition a high yield point. It thus provides a material of special value for turbine blading where high steam temperatures and pressures have to be met.[5]

A particularly high resistance to sulphuric acid is given by a 14-18-4-4 Cr-Ni-Mo-Cu steel.[5]

The 6-10 Cr 3-4 Si alloy possesses excellent resistance to oxidation up to a temperature of about 900 deg. C. but has no great mechanical strength at high temperatures. This steel is essentially used for internal combustion engine valves.[5]

An idea of the corrosion-resistance of the various types



Two 600-Gal. Vacuum Holding Tanks Fabricated of 18-8 Stainless Steel for Use in Processing and Storing of Orange Juice in the Plant of a Leading California Producer.

of alloys to many media is given by Critchett[29] in Table III. This table is based largely on laboratory experiments performed in all parts of the world as they have been confirmed by experience with actual plant installations. Hatfield[5] and Norlin[11] also give British and Swedish experience with alloy steels.

Resisting Stress at High Temperature

The increase in working temperatures in high-pressure steam plant calls for materials capable of resisting stress at high temperatures, of retaining their strength for long periods, and of resisting chemical attack by air, flue gases and super-heated steam. Jenkins, Tapsell, Mellor and Johnson[8] report work carried out at the National Physical Laboratory on the effect of 0.5 and 1 per cent Mo on creep and on resistance to flue gas. These steels are markedly affected by heat treatment. The creep rate of a spheroidized steel with 0.11 per cent C and 0.52 per cent Mo at 550 deg. under a load of 20,000 lbs. per sq. in. is 80 times that of the oil-quenched and tempered specimen. Heat treatment at 550 deg C. for four months before applying the load caused a slight improvement in resistance. With a steel containing 0.4 per cent C, however, oil-quenching and tempering reduced the creep resistance below that of the air-cooled condition. Little difference was found in the rate of corrosion of the several steels in a synthetic flue gas containing 0.04 or 0.07 per cent sulphur dioxide, but the attack was much more rapid at 600 than at 500 deg. C. Super-heated steam also attacks all the steels at about the same rate. In both instances the texture of the scale produced is an important factor.

The use of high temperatures and pressures in chemical synthesis has been covered very comprehensively by Sarjant and Middleham.[6] At present the use of high pressures on the largest scale is in the production of synthetic ammonia and in the hydrogenation of coal and tars for the production of motor fuels. Besides the commercial development of high-pressure processes adapted to the fertilizer, oil, and coal industries, a vast amount of research is being devoted to the systematic study of organic chemical reactions by this means. Practically all of these processes involve the exposure of the material to hydrogen at high temperatures and pressures.

Metals Susceptible to Hydrogen

Metals are susceptible to hydrogen diffusion and at higher temperatures to hydrogen embrittlement or attack. Sarjant and Middleham have assembled a summary of the principal published results (on some 72 steels) in tabular form. Their own experiments consisted of the exposure of 11 steels (all forged except steel G which was both forged and cast) to hydrogen for 5400 hrs. at 325 deg. C. and under 125 and 250 atmospheres pressure; 710 hrs. at 450 deg. C. and under 125 and 250 atms. pressure; 1,027 hrs. at 450 deg. C. and under 250 atms. pressure; and 1,048

Table III—Pure Media and Conditions for Practically Complete Corrosion Resistance of Various Low-Carbon Stainless Steels

Media	Conc., per cent	Temp. C.	Percentage of alloying elements: 13 Cr	18 Cr	25 Cr	Cr-Mn-Cu 18-8-1	Cr-Ni 18-8	Cr-Ni 25-20	Cr-Ni-Mo-Cu 18-8-2.5-1.5
HNO_3	10	20	x	x	x	x	x	x	x
H_3PO_4	10	20	x	x	x	x	x	x	x
Formic	10	20	x	x	x	x	x	x	x
Acetic	10-50	20	x	x	x	x	x	x	x
Acetic	Glacial	20	x	x	x	x	x	x	x
Tannic	10	100	x	x	x	x	x	x	x
Phenol	10	100	x	x	x	x	x	x	x
Na_2CO_3	10	100	x	x	x	x	x	x	x
Pb acetate	25	100	x	x	x	x	x	x	x
KNO_3	50	100	x	x	x	x	x	x	x
Cr_2SO_4	Sat.	100	x	x	x	x	x	x	x
$ZnCl_2$	1.2 d.	20	x	x	x	x	x	x	x
HNO_3	30	20	....	x	x	x	x	x	x
Formic	30	20	....	x	x	x	x	x	x
Citric	10	20	....	x	x	x	x	x	x
NH_4NO_3	Sat.	100	....	x	x	x	x	x	x
Atmospheric	General	...	....	x	x	x	x	x	x
Atmospheric	Under	900	....	x	x	....	....	x	....
HNO_3	10	100	....	x	x	x	x	x	x
HNO_3	Conc.	20	....	x	x	x	x	x	x
Atmospheric	Above	900	....	....	x	....	....	x	....
Furnace gases	Under	900	....	....	x	x	....	x	....
Mine waters		20	....	....	x	....	....	x	....
Sulphur-compound gases	Under	900	....	....	x	x	....	....	....
Flue gases	....	...	....	....	....	x	x	x	x
Mineral waters	(S)	20	....	....	....	x	....	....	....
Lactic	1.5	100	....	....	....	x	x	x	x
Oxalic	10	20	....	....	....	x	x	x	x
Salt spray	....	20	....	....	....	....	....	x	....
Furnace gases (reducing)	....	950	....	....	....	....	....	x	x
Sulphite liquors	....	...	....	....	....	....	....	....	x
Sea water	....	...	....	....	....	....	....	....	x
$FeCl_3$	Low	20	....	....	....	....	....	....	x

hrs. at 550 deg. C. and under 125 and 250 atms. pressure with results as follows.

Steel A (0.22% C steel) suffered severe intergranular cracking, even at the comparatively low temperature of 325 deg. C. when the pressure of the hydrogen was 250 atms. At 125 atms. pressure the severity of the attack was definitely reduced.

Steel B (2.5% Cr, 0.26% C) did not suffer hydrogen attack up to 550 deg. C. and under 125 atms. but it was seriously embrittled at this temperature and at 450 deg. C.

Steel C (1% Cr, 0.21% V, 0.40% C) was not adversely affected at 325 deg. C. and 250 atms. At 550 deg. C. it was embrittled, but the effect of the hydrogen at this temperature in the experiments carried out at 125 atms. only amounted to slight partial decarbonization.

Steel D (1.58% Cr, 1.15% Al, 0.23% Mo, 0.31% C) was unaffected by hydrogen, apart from slight decarbonization, up to 550 deg. C. at 125 atms. possibly as a result of the aluminum content. It suffered little embrittlement from the effects of prolonged heating. Nitriding reduced the amount of decarbonization, but introduced a susceptibility to intergranular crackings.

Steel E (2.31% Ni, 0.48% Cr, 0.93% Mo, 0.30% C) under the higher pressure of 250 atms. showed only slight hydrogen attack at 550 deg. C. which was confined to the portions of the test vessel cold-worked by machining. Some impairment of shock-resisting properties resulted, but the measure of this effect was probably not sufficient to render it unsuitable under these conditions for autoclave uses, where subjection to shock is generally absent. At 750 deg. C. hydrogen attack was found to be severe.

Steel F (0.32% Cu, 0.27% Cr, 0.84% Mo, 0.14% C) was immune from any deterioration up to 550 deg. C. and under 250 atms. Short exposure to 750 deg. C. under the same pressure however, produced serious intergranular cracking.

Steel G (6% Cr, 0.55% Mo, 0.24% C) was free from attack by hydrogen, but suffered embrittlement at 450 and 550 deg. C. under 250 atms. pressure. The short exposure at 750 deg. C. had not caused hydrogen penetration and restored the toughness lost during prolonged exposure at 450 deg. C. At 550 deg. C. the cast material did not suffer any loss of such toughness as it possessed initially.

Steel H (13% Cr, 0.12% C) was completely free from hydrogen attack under the most extreme conditions applied in these experiments, but suffered some slight embrittlement at 325 deg. C. and at 550 deg. C.

The more highly alloyed austenitic steels I (18-8 Cr-Ni, 0.12% C), J (18-8-2-0.6 Cr-Ni-Mo-Ti) and K (25-18-1.19-0.13 Cr-Ni-Mn-C) gave no indications of hydrogen attack or embrittlement in the range of temperatures and pressures employed.

Corrosion Resistant Cast Irons

Three papers dealing specifically with cast irons, Pearce[7], and Maxwell [10, 28] cover the difficulties encountered with gray cast iron and the development of low-alloy, wear-resistant, high silicon, and austenitic cast irons. Low-alloy cast irons, widely used for caustic service, have the following compositions: (1) 3.5% C, 0.50% Si, 2% Ni, 0-0.30% Cr, 0.50% Mn, (2) 3.30% C, 0.70% Si, 1.50% Ni, 0.60% Cr, 0.50% Mn. A cast iron for use in chemical manufacturing equipment in which the metal is exposed to abrasive wear has the composition 2.75-3.6% C, 4.40-4.6% Ni, 1.40-1.6% Cr, 0.50-1.5% Si, 0.20-0.7% Mn. For resistance to scaling in sulphurous atmospheres where the material is not subject to shock, a 4-5 per cent Si—2 per cent Cr alloy has been successfully used. The 13 to 16 per cent Si cast iron, which has been used for resistance to sulphuric and nitric acid for many years, has been recently improved by the addition of 3 to 4 per cent Mo and 0.25 per cent Ni to increase its resistance to hydrochloric acid. The austenitic cast irons, of the type compositions given in Table IV[28], are used for resistance to heat and corrosion. Such applications in chemical-process equipment as rotary and reciprocating pumps, valves, pipe lines, and reaction vessels operating on sulphuric acid mixtures, caustic and many salts. Under high temperatures the austenitic cast irons have shown excellent performance in resistance grids, coke-oven door frames, heat-treating stands in annealing furnaces, thermocouple sheaths, and similar applications.

Table IV—Composition of Austenitic Cast Irons

	Regular Ni-Resist	Ni-Resist (copper-free)	Nicrosilal	Causal
Nickel	12.0-15.0	15.0-20.0	18.0	18.0-21.0
Chromium	1.25-4.0	2.50 (max.)	2.0	1.5
Carbon	2.75-3.1	2.0-2.3	1.8	2.3
Silicon	1.5-2.0	0.6-2.0	6.0	2.2
Manganese	1.0-1.5	1.0-1.5	1.0	1.10
Copper	5.0-7.0	.....	...	4.5
Sulphur	0.10 max.	.....	...	0.05 (max.)

Other installments of this valuable correlated abstract will appear in later issues, dealing with other phases and fields.—EDITOR.

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Intercrystalline Cracking of Steel

IN AQUEOUS SOLUTION

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This investigation is conducted under a cooperative agreement between the Joint Research Committee on Boiler Feedwater Studies and the United States Bureau of Mines. It is supervised by a subcommittee of which J. H. Walker is chairman, and is carried out at the Eastern Experiment Station of the Bureau of Mines, at the University of Maryland, College Park, Md.

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STATISTICAL INVESTIGATION OF WATER conditions existing in boilers suffering intercrystalline cracking, and early experimental work indicated that this type of failure was primarily caused by sodium hydroxide. Further study over a period of years brought forth a number of facts and results that could not be explained by this relatively simple conception, and finally led to the discovery that at 250 deg. C. very small amounts of sodium silicate in the sodium hydroxide greatly influenced the cracking. As a result of this discovery, a tendency existed to make the tacit assumption that the action of sodium hydroxide-sodium silicate or very similar solutions would serve to explain the production of intercrystalline cracks under all conditions, and complete exploration of their attack would make it possible to correlate all the experimental facts.

This viewpoint again appears to be too simple. The experimental results in this paper indicate that the cracking depends to a marked extent on the surface conditions produced on the steel and may, therefore, be influenced by as many factors as encountered in the corrosion of steel. It has been found that intercrystalline cracking can be produced in sodium hydroxide solutions containing a number of substances other than sodium silicate, and moreover that the particular agent which must be added to the sodium hydroxide depends on the temperature and conditions of the test. Certain chemicals may be substituted for the sodium hydroxide itself, such as sodium nitrate, or strangely enough, a dilute nitric acid solution.

This discussion treats: First, tension tests in sodium hydroxide solutions at 250 deg C.; second, intercrystalline cracking in sodium nitrate solutions; third, intercrystalline cracking in sodium hydroxide solutions; fourth, inter-

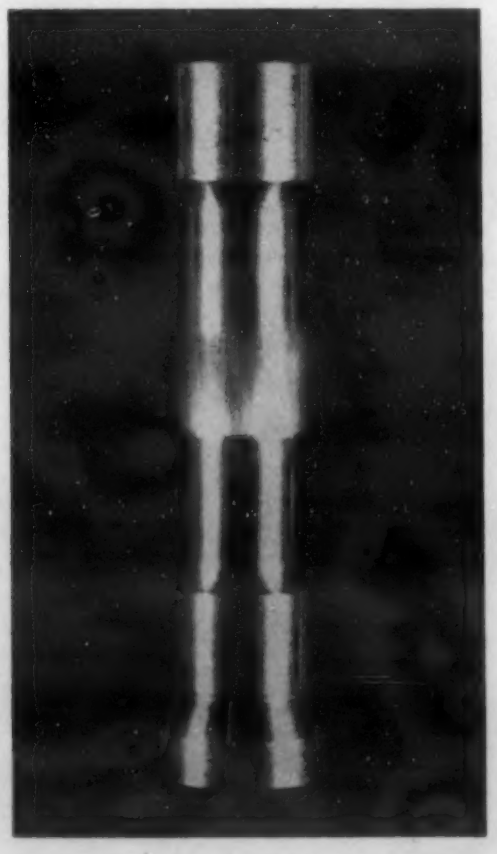


Fig. 1.—Tubular, Concentric Ground Specimen Made of Boiler Flange Steel.

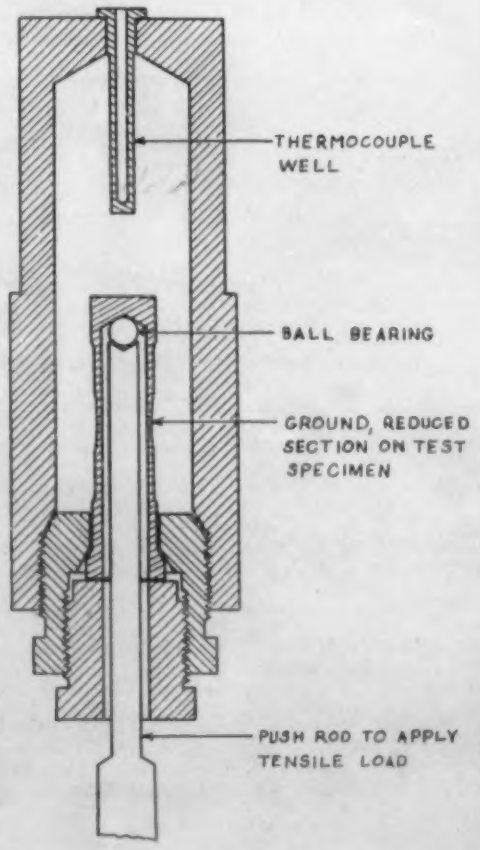


Fig. 2.—Tension Test Bomb and Specimen.

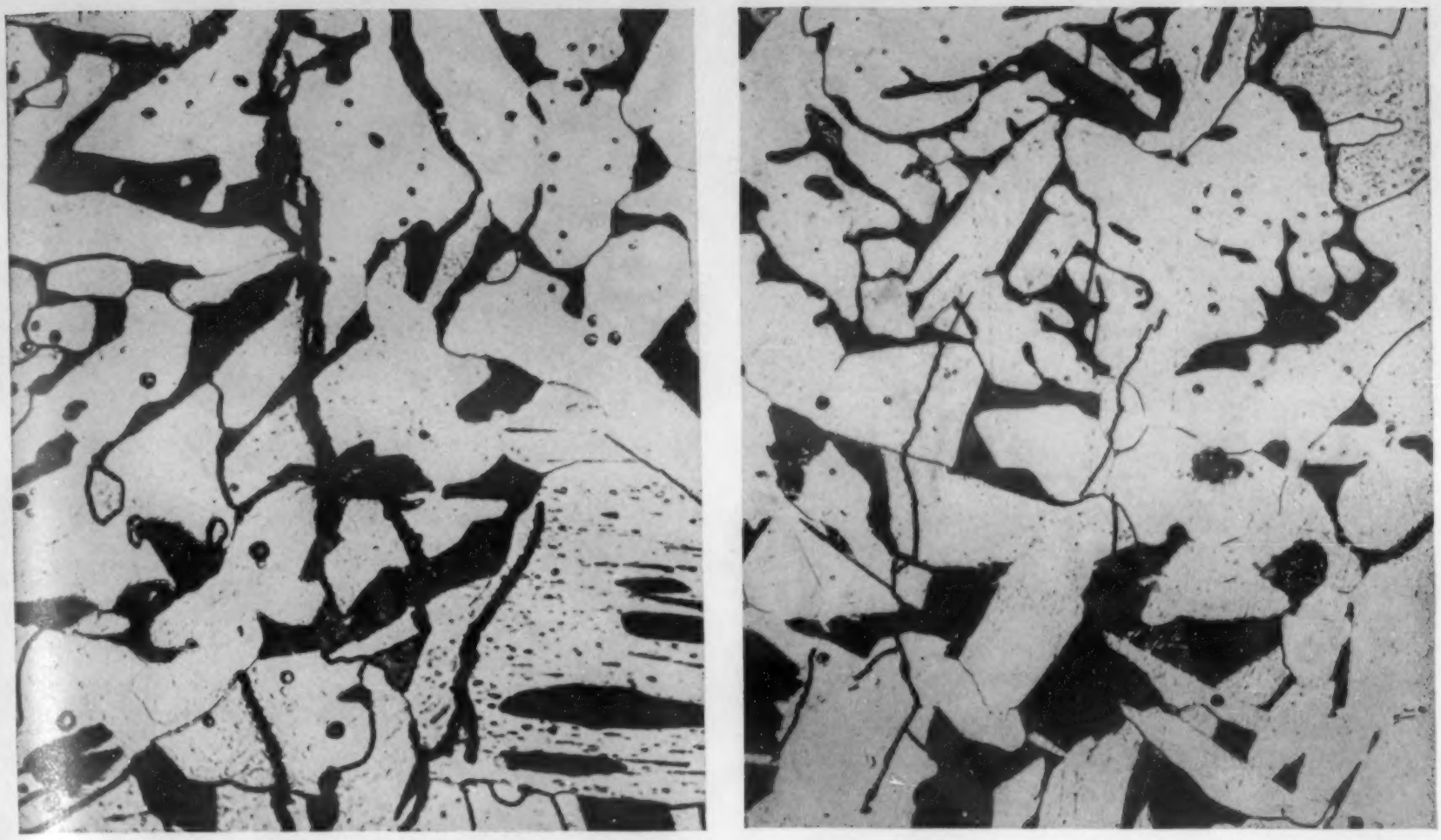


Fig. 3.—Cracks Produced in Concentric Ground Boiler Flange Steel Specimens by Sodium Hydroxide-Sodium Silicate (left) and Sodium Hydroxide-Antimony Chloride (right) Solutions at 250 deg. C. Both etched with 1 per cent nital. Magnification 500 X.

Solution	g./100 g. H_2O
NaOH	25
Na_2SiO_3	0.32
NaCl	0.3

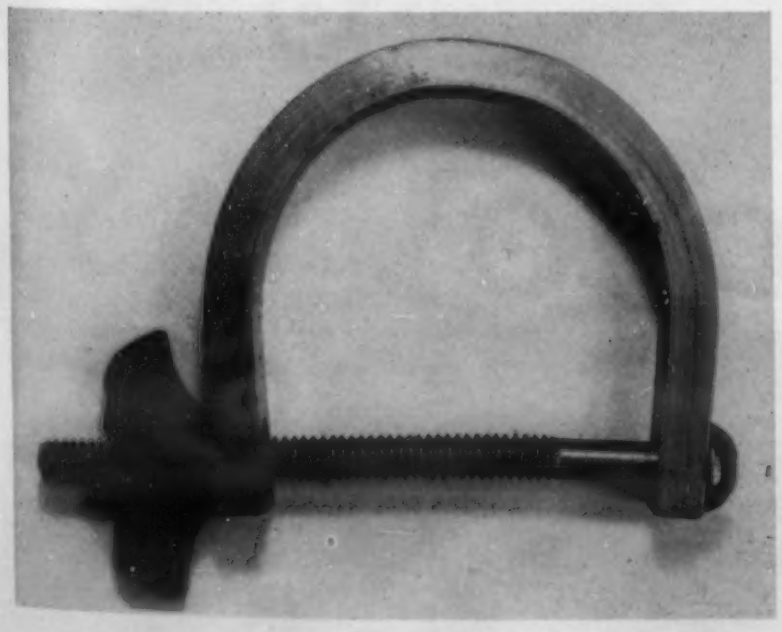
Solution	g./100 g. H_2O
NaOH	25
$SbCl_3$	2.0
NaCl	4.8

crystalline cracking in nitric acid solutions, and finally, the conclusions expressing a viewpoint which seems to correlate best the information now available on this type of failure.

Tension Tests in Sodium Hydroxide Solutions

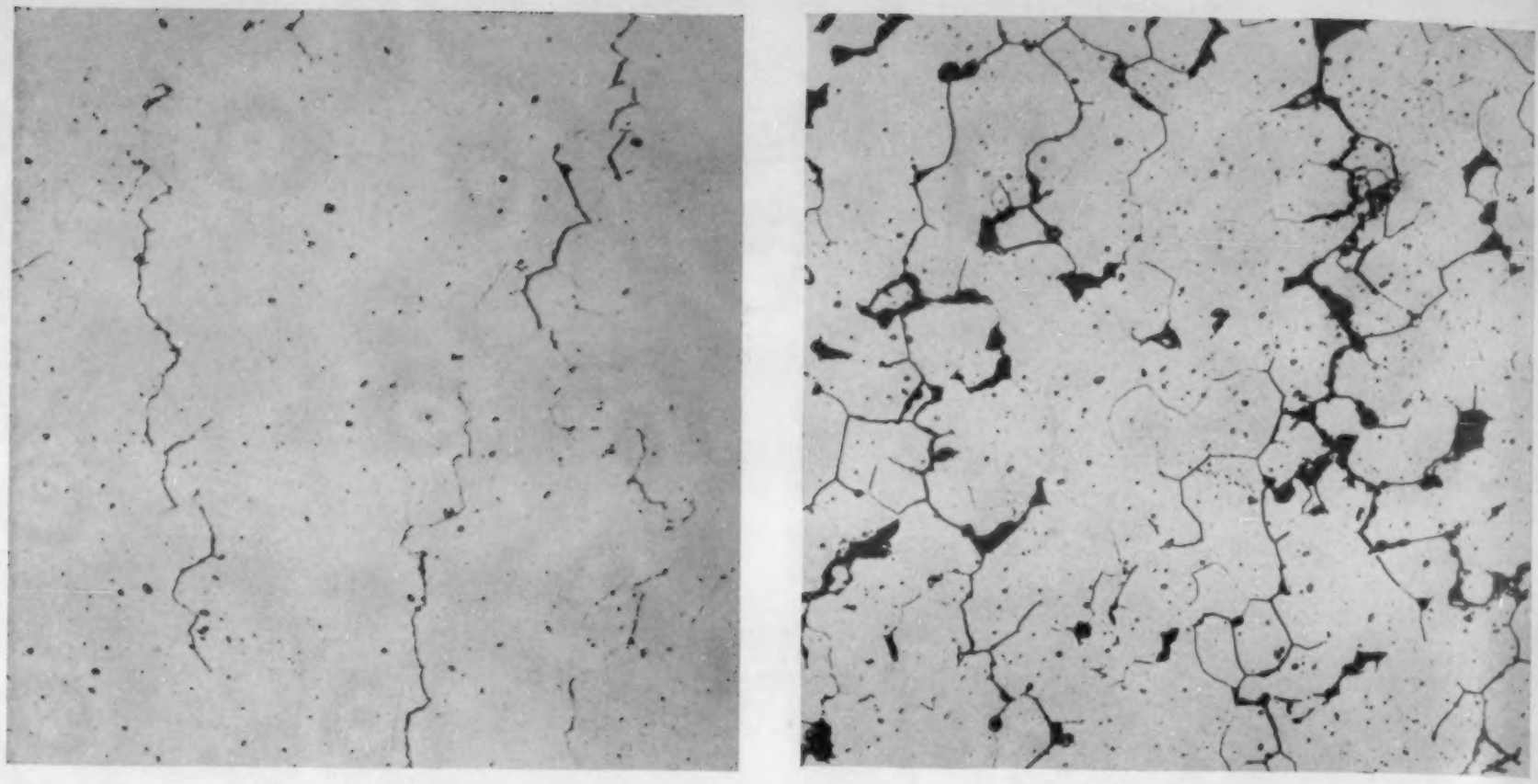
A series of tests carried out at 250 deg C. have indicated that the load carrying ability of the concentric ground specimen shown in Fig. 1 could be reduced from 75,000 to 50,000 lb. per sq. in., by the action of sodium hydroxide-sodium silicate solutions. The specimen made of boiler flange steel is tubular, closed at the top and held in the bomb as shown in Fig. 2. The tensile load is applied by a push rod passing up through the center and connecting to an accurate weight and lever system. The equipment, the steel used, procedure and results of these tests have already been described in two papers.[1, 2]

Fig. 4.—"U" Bend Specimen Ready for Immersion in the Solution.



The results in Table I show that either titanium oxide, germanium oxide, or antimony salts may be substituted for sodium silicate to produce cracking of the steel. The titanium oxide lowered the load carrying ability of the concentric ground specimens almost as much as sodium silicate; the antimony oxide produced failure at 65,000 lb. per sq. in., and, while the germanium oxide did not produce failure of the steel, definite cracking was evident. The solubility of titanium oxide may be very low, but a sufficient concentration was attained in the solution to decrease the load carrying ability. Spectrographic analysis of this oxide indicated only a trace of silica.

Fig. 3 compares the cracks produced in sodium hydroxide-sodium silicate solutions with those produced in sodium hydroxide-antimony chloride solution. The specimens were etched quite deeply to indicate the position of the cracks with respect to the grain boundaries. The cracks run vertically through the pictures, following the boundaries in some cases but cutting across through pearlite and into ferrite grains in others. The cracks in the antimony solution are somewhat narrower than those in the sodium silicate but this is largely a result of the area selected for



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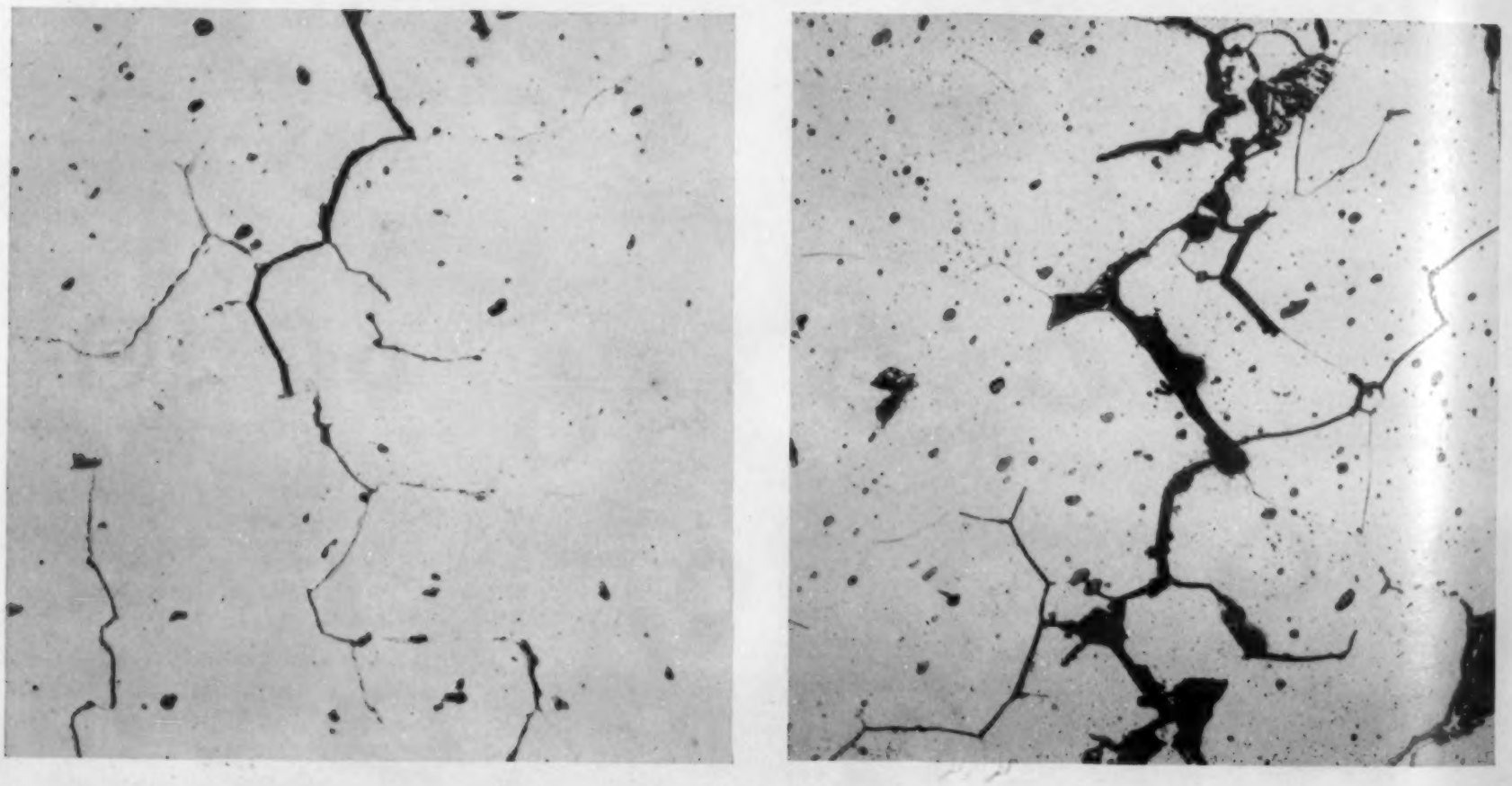


Magnification 500 X

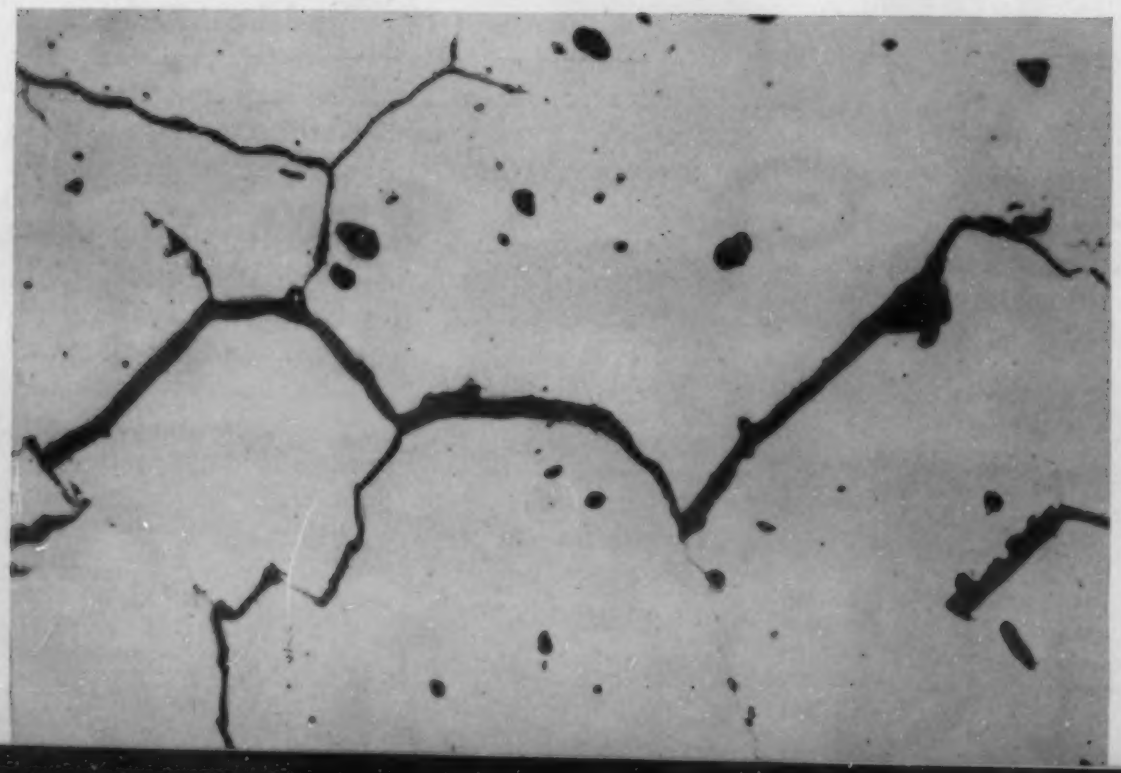


Fig. 5.—Intercrystalline Cracks Found in Test Bomb. Photomicrographs at left are unetched; the two at right are etched with 1 per cent nital.

Magnification 1000 X.

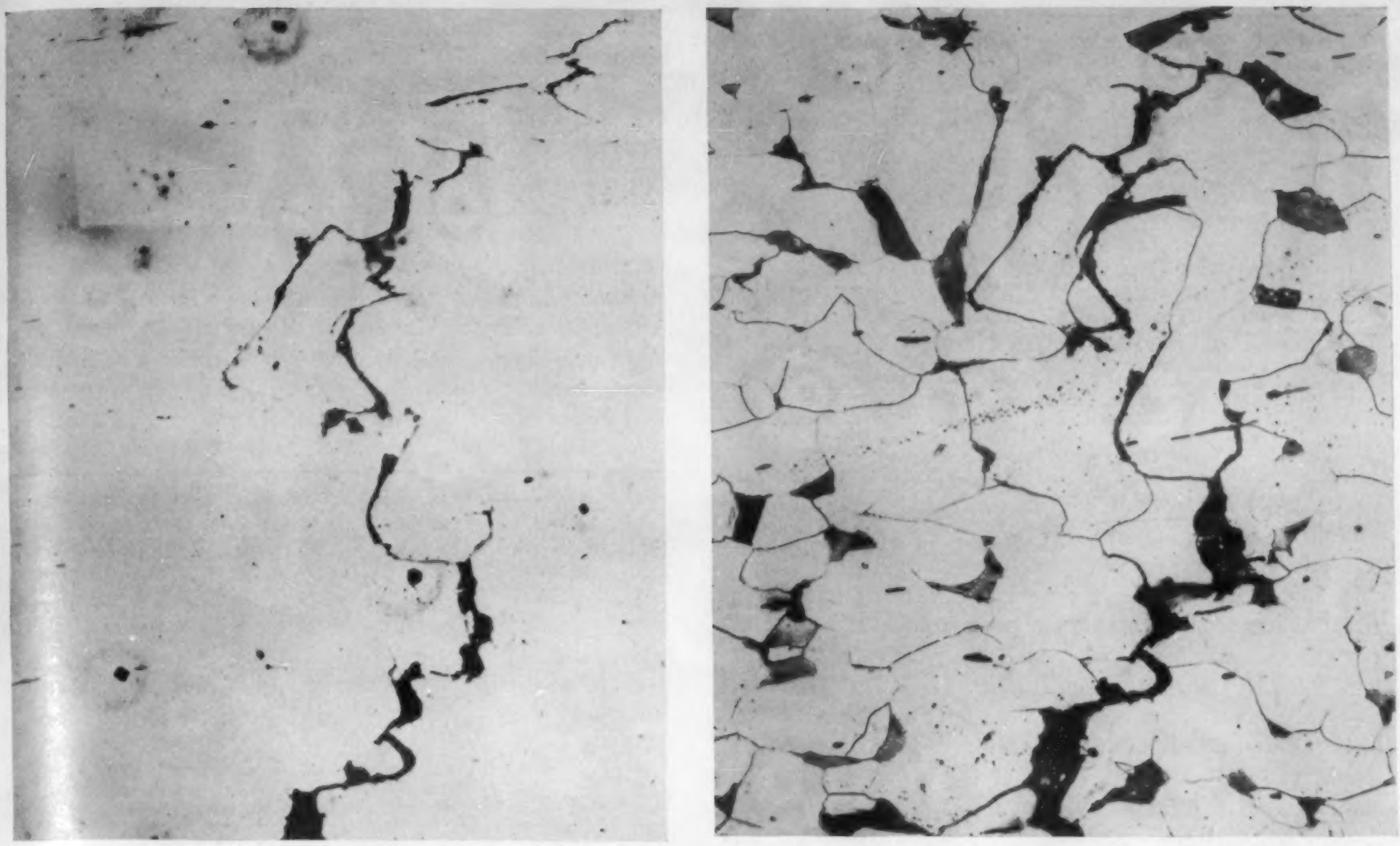


Fig. 6.—Intercrystalline Cracks Produced in Cold Rolled and Boiler Flange Steel by Nitrate-Manganese Solutions: All magnifications 500 X. The ones at left are unetched, and those at right etched with nital. Cold rolled steel at top and boiler flange steel at bottom. Test solution contained 120 g. $NaNO_3$ and 0.3 g. $MnCl_2$ per 100 g. H_2O.

Table I.—Failure of Concentric Ground Specimens in Sodium Hydroxide Solutions Containing Titanium Oxide, Germanium Oxide, or Antimony Salts

Baker's Chemically Pure Sodium Hydroxide. Temperature 250°C. Specimens of Boiler Flange Steel. All loads applied at 250°C.

Specimen Number	Load lb. per sq. in.	g./100 g. H_2O NaOH	NaCl	Added Comp.	Conc.	Failure hrs.	No Failure Days
18.16	70,000	25	..	TiO_2	1(a)	96	..
18.20	60,000	25	0.5	TiO_2	1	176(b)	..
18.23	55,000	25	0.5	TiO_2	0.5	186(b)	..
18.26	50,000	25	0.3	TiO_2	0.5(c)	.....	31
29.27	60,000	25	0.3	GeO_2	0.32	.....	15(d)
29.28	65,000	25	0.3	Sb_2O_3	0.32	81(b)	..
29.29	60,000	25	4.8	$SbCl_3$	2.0	.....	10(d)

(a) Solubility of titanium oxide in sodium hydroxide unknown.
(b) Failure at shoulder of specimen.
(c) Bomb rotated at 250°C. before test to insure saturation with TiO_2.
(d) Microscopic examination indicated intercrystalline cracks.

photography. Microscopic study indicates that these solutions, under the exisitng experimental conditions, produce quite similar cracking which is by no means completely intercrystalline.

In these tension tests the steel is under relatively high stress and as soon as some grain boundaries have been penetrated, failure in the remaining sound steel tends to occur in a normal, transcrystalline manner. It is now believed that the high stress accounts for the type of failure shown in Fig. 3 and the difference between this cracking and that shown in the following sections of the paper may be due more to the mechanical difference in method of loading than to any essential difference in type of chemical action.

Intercrystalline Cracking in Sodium Nitrate Solutions

For a number of years it has been known that intercrystalline cracking could be produced in solutions containing high concentrations of sodium nitrate as well as those containing sodium hydroxide. German investigators[3] have recently reported the rapid intercrystalline cracking of steel in hot nitrate solutions, and apparently have not encountered difficulty in producing this type of failure.

Four tension tests at 250 deg. C. with sodium nitrate solutions, as shown in Table II, did not result in failure. The sodium chloride was added because it has generally been found to accelerate the solution attack. The seven U-bend tests in Table III with sodium nitrate from three different sources did not cause cracking of the steel. These results are not in agreement with those reported in the literature[4] or with recent German investigations.

The U-bend specimens for the tests in Table III were made of cold rolled (S.A.E. 1020) strip steel. They were flat bars 1/4 x 1/2 in., bent around rods of various diameters up to 2 1/4 in., and drawn together by a bolt and wing nut to retain as high an elastic stress in the steel as possible. Fig. 4 is a picture of one of the U-bend specimens ready for immersion. At least two of these specimens were used in each test. The solutions were kept

Table II.—Resistance of Concentric Ground Specimens to Failure in Sodium Nitrate Solutions.

Temperature 250°C. Specimens of Boiler Flange Steel. All loads applied at 250°C.

Specimen Number	Load, lb. per sq. in.	g./100 g. H_2O $NaNO_3$	NaCl	No Failure Days
7.13	70,000	34	0.5	10
7.11	60,000	34	0.5	10
18.2	60,000	50	0.5	10
18.8	60,000	120	0.5	10

boiling under condensers at atmospheric pressure and loss of water through vaporization normally varied from 0 to about 5 per cent each 12 hours. This loss was made up by the addition of distilled water twice a day. The solutions containing 25, 50, and 100 grams of sodium hydroxide per 100 grams of water had approximate boiling points of 109, 120, and 146 deg. C., respectively.

At this stage in the experimental work one of the bombs shown in Fig. 2 was found cracked from a point two or three threads below the seat on the large nut to the top of the solution level. The crack had penetrated to a uniform depth of about 13/32 in. through its entire length, indicating that the concentration of stress near the bottom seat was not of importance in its propagation. The stress in

Table III.—Resistance of "U" Bend Specimens to Cracking in Boiling Sodium Nitrate Solutions.

Temperature 100-110°C. Specimens of Cold Rolled Steel(a)

g./100 g. H_2O $NaNO_3$			No Crack Days
60	C. P.(b)	.....	3
100	C. P.	.....	3
120	C. P	.....	3
120	Chile(c)	.....	3
Excess Solid	Chile	.....	3
100	Grasselli(d)	.....	3
120	Grasselli	.....	3

(a) In all tables S.A.E. steel 1020 is indicated.
(b) C. P.—Baker's chemically pure sodium nitrate.
(c) Chile Saltpetre—imported.
(d) Grasselli nitrate—commercial.

the metal due to steam pressure was well below 1000 lb. per sq. in. The authors believe that this failure probably occurred at an applied stress below two or three thousand pounds per square inch, although the internal stress in the metal may have been high.

The bomb was bored on a lathe from a hot rolled bar of low carbon steel secured from a commercial warehouse supplying bar stock.

This failure was of great interest, especially in view of the lack of agreement existing in the experimental results with the nitrate solutions, and it was subjected to careful metallographic examination. The photomicrographs in

Table IV.—Rapid Cracking of "U" Bend Specimens in Boiling Nitrate-Manganese Solutions.

Baker's Chemically Pure Sodium Nitrate. Specimens of Cold Rolled Steel.

g./100 g. H_2O $NaNO_3$	NaCl	Added Manganese Salt	Conc.	Crack Days
120(a)	..	$MnSO_4$	Small amount	1/4
120	1.0	$MnSO_4$	0.4	1
120	1.0	$MnSO_4$	0.4	1
120	..	$MnSO_4$	0.4	1
120	1.0	$MnSO_4$	0.4	1(b)
120	1.0	$MnSO_4$	0.4	1(c)
120	1.0	$MnSO_4$	0.4	1(d)
120	..	$MnCl_2$	0.4	1
50	..	$MnCl_2$	0.2	3
25	0.3	$MnCl_2$	0.3	No cracks
25	0.3	$MnCl_2$	3.0	No cracks
50	..	$KMnO_4$	0.25	1
120	..	$MnCl_2$	0.02	9(e)

(a) Chile Saltpetre.
(b) Specimen made of boiler flange steel 1/8" thick.
(c) No applied stress-cracks appeared on inside of bend.
(d) Cold rolled, annealed, and polished specimens all broken in this test.
(e) Only one specimen cracked.

Fig. 5 are cross sections of the crack at three different magnifications in the unetched and etched condition. The etched sections show 100 per cent intercrystalline cracking and this was also true of all the other areas studied under the microscope. The crack is definitely more intercrystal-

line than those in Fig. 3 or any cracks that have been reported in pure sodium hydroxide-sodium silicate solutions. The absence of high applied stress may explain the development of these cracks in a completely intercrystalline manner. The width of the fine cracks have been estimated at 5 or 10 one-millionths of an inch from the photomicrograph at 1000 X.

It was at first believed that this failure was due to sodium hydroxide, but the last 10 or 12 tests in the bomb were made with a sodium nitrate solution and it will be shown later that either the hydroxide or nitrate or mixtures of the two may have been responsible.

The peculiar intercrystalline nature of these cracks, the fact that it had not been found possible to exactly reproduce them experimentally in any solution, and the discrepancies still existing in the work of various investigators resulted in a further intensive study of the action of both sodium nitrate and sodium hydroxide solutions.

Additions of ferrous sulphate, uranium acetate, cerium oxide, sodium chromate and copper sulphate to boiling concentrated sodium nitrate solutions did not produce cracking of U-bend specimens. When a trace of manganous sulphate was added, the first specimen in Table IV was cracked almost through in many places in 5 or 6 hrs. The remaining tests in Table IV show that manganous sulphate or chloride or potassium permanganate could be added to the sodium nitrate to produce cracking. Fifty grams of sodium nitrate per 100 grams of water cracked the steel, but 25 grams did not. The last test indicates that decreasing the manganous chloride content to 0.02 gram per 100 grams of water increased the time required for failure from less than 1 to 9 days. In this test only one of the two specimens was cracked, whereas in all the other tests both specimens were cracked. Specimens of cold rolled, cold rolled annealed and boiler flange steel all developed fissures and it made little difference whether the surface of the cold rolled steel was machined, left as rolled, or polished with No. 00 emery cloth.

Fig. 6 contains four photomicrographs of cracks produced in sodium nitrate solutions in cold rolled and boiler flange steel. They are completely intercrystalline and comparison with Fig. 5 indicates no difference from those found in the bomb.

Fig. 7 is a picture of one of the specimens used in the sixth test in Table IV. It was made of cold rolled steel bent to a short radius. The ends were not pulled together by a bolt and no external load was applied in any way so that all the stress that the steel suffered must be internal, resulting from cold work, manufacture, or heat treatment. After boiling in the solution for three days it was badly cracked; not on the outside, but on the inside of the bend, the cracks extending some distance down the sides as shown in Fig. 7. They were completely intercrystalline and normal to the edge of the specimen at the center of the radius, changing gradually to about a 30-degree angle with respect to the edge as they moved down the side.

It may at first appear that the inside of the bend was under compressive stress and that the cracking did not occur in the area of the specimen under tension. This may not, however, be the case, for after the load that was applied to produce bending was released, the reacting forces in the steel would probably tend to produce an internal tensile stress on the inside of the bend and a compressive stress on the outside.

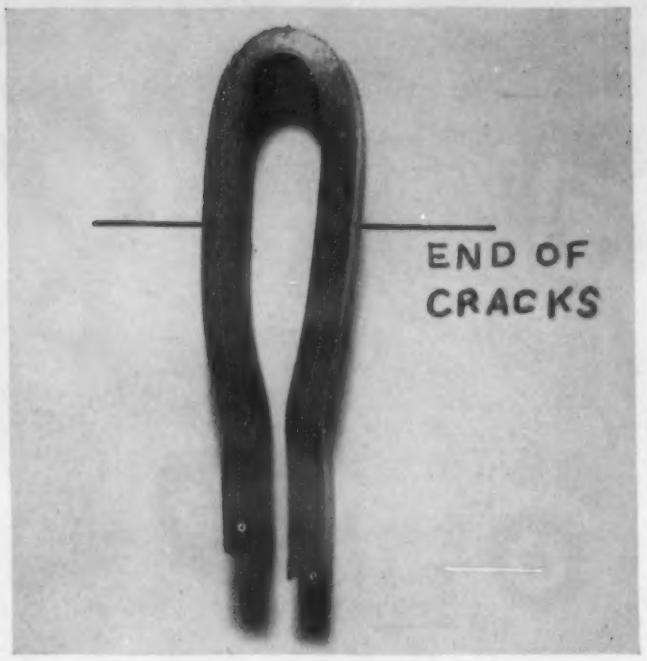


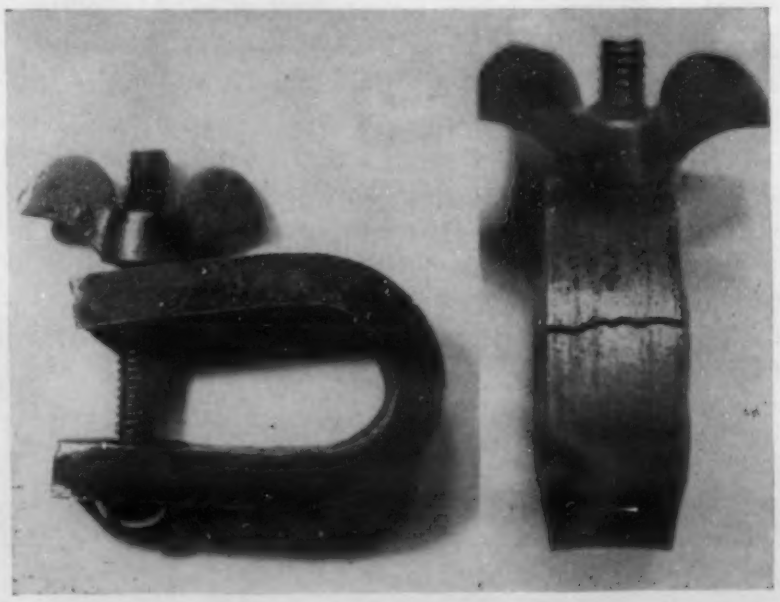
Fig. 7.—"U" Bend Specimen of Cold-Rolled Steel Cracked on Inside of Bend without Applied Stress.

The failure of this specimen adequately demonstrates that intercrystalline cracking can occur whether the steel is under applied external stress above the yield point or not. Internal stress resulting from cold work or other treatment may cause rapid cracking in the complete absence of external forces.

The concentrated sodium nitrate solutions used in these tests do not discolor or change the visual appearance of the surface of the steel at all, yet within one day they can crack through a ¼ or 5/16-in. section in several places. Preliminary tests indicate that these nitrate-manganese solutions cause a considerable increase in the manganese content at the surface of the steel but this fact must be investigated further. Manganese compounds are not the only ones that will produce cracking in the sodium nitrate solutions for the addition of titanium chloride to a nitrate solution produced a similar result in about 6 days. Further study may reveal other compounds that exert the same influence.

The rapid intercrystalline cracking produced in these U-bend specimens should eliminate the belief that fatigue or corrosion fatigue is a necessary factor in this type of failure. Repeated stress may accelerate the ultimate parting of the metal, but cracking will readily occur in its entire absence.

Fig. 8.—"U" Bend Specimen of Boiler Flange Steel Broken in One Day by Nitrate-Manganese Solution.



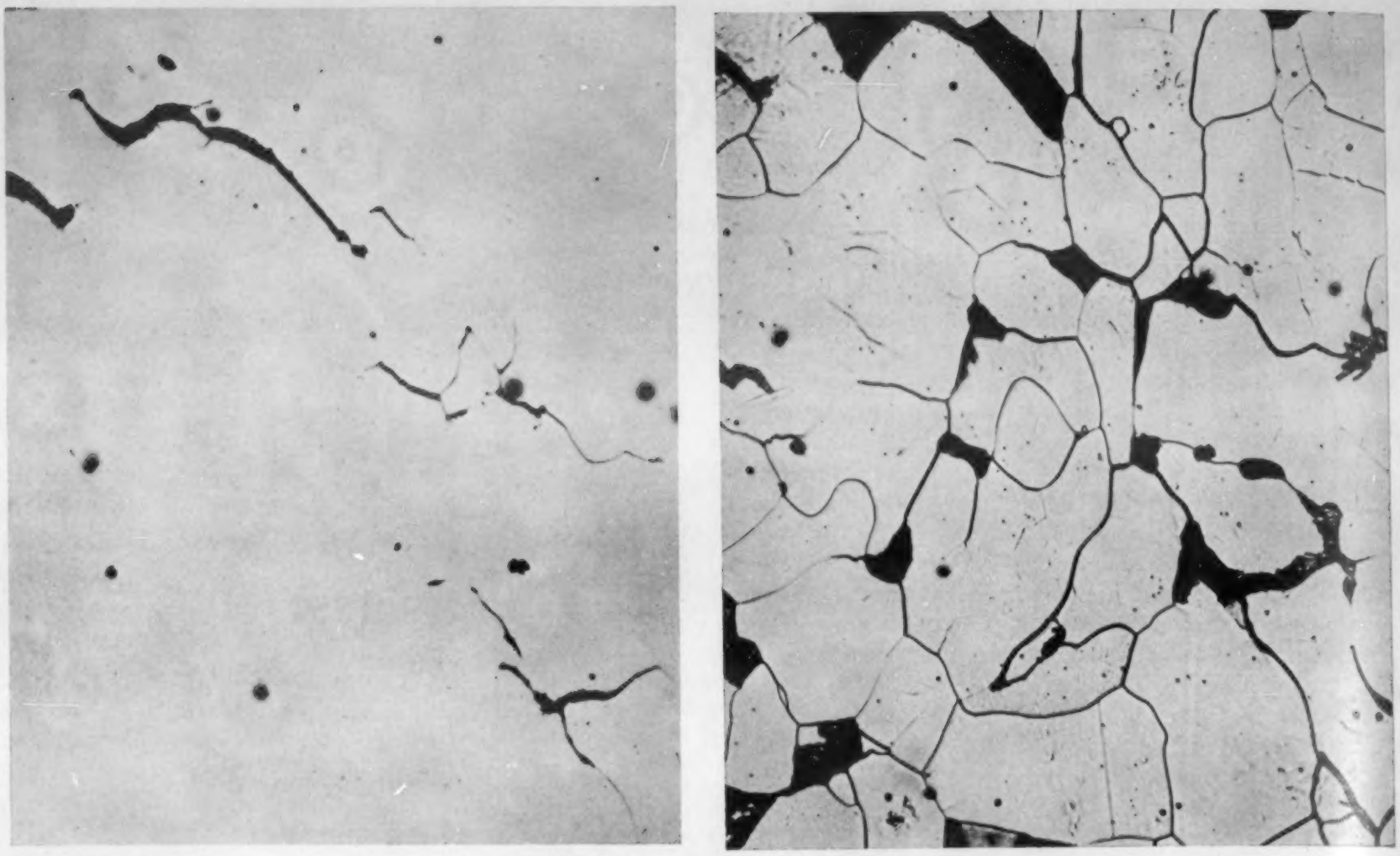


Fig. 9.—Intercrystalline Cracks Produced in a "U" Bend Specimen of Boiler Flange Steel by a Sodium Hydroxide-Sodium Nitrate Solution.

Solution	g./100 g. H_2O
NaOH	50
$NaNO_3$	0.2
NaCl	0.2

Both are at magnification of 500 X. The one at left was unetched and the other was etched with nital.

Fig. 8 shows two views of a U-bend specimen made of boiler flange steel that cracked entirely through a 5/16-in. section within one day. The specimen is shown just as it was removed from the solution.

These U-bend tests make an excellent, simple demonstration of the rapid damage which intercrystalline attack can produce in a steel specimen. To those people who do not believe that this form of solution action on the metal is serious the authors would suggest the following experiment:

Bend a ½ by ¼-in. bar of cold rolled (S.A.E. 1020) steel into a "U" on a bar 2¼ in. in diameter and draw the ends together about 1 in. with a bolt as shown in Fig. 4. Put two of these specimens in a beaker with 300 c.c. of a solution containing 120 grams of $NaNO_3$ and 0.2 gram of $MnCl_2$ per 100 grams of water. The top of the beaker should then be closed with a very large rubber stopper that does not touch the solution and that is connected to a condenser. With the solution boiling slowly the specimens should be cracked in many places within 48 hours.

Intercrystalline Cracking in Sodium Hydroxide Solutions

The interesting results, secured in the concentrated sodium nitrate solutions after the addition of manganese salts had been found to cause intercrystalline cracking, led to further investigation to produce similar damage in U-bend specimens in sodium hydroxide solutions.

It has been indicated in this report that sodium hydroxide-sodium siicate solutions have not yet been found to cause intercrystalline cracking exactly similar to that shown in Figs. 5 and 6. Table V shows a series of tests with U-bend specimens in boiling sodium hydroxide and sodium hydroxide-sodium silicate solutions that did not produce cracking of any kind. In 1921 Jones[4] reported and showed pictures of completely intercrystalline cracks produced in steel by solutions of potassium hydroxide, and similar results have been reported at various times since 1921. The purity of the solutions used in these tests is not known, but at the present time the results in Table V indicate that if impurity was present it may have been something other than sodium silicate.

Table V.—Resistance of "U" Bend Specimens to Cracking in Boiling Sodium Hydroxide-Sodium Silicate Solutions.

Technical Sodium Hydroxide(a). g./100 g. H_2O		Specimens of Cold Rolled Steel. No Crack Days
NaOH	$NaSiO_3$	
5	..	7
25	..	7
50	..	7
100	..	7
25	0.5	7
50	0.2	6
50	0.5	6
50	1.5	6
50	5.0	6
50	15	6
100	1.0	7
100	5.0	7

(a) Flake caustic furnished by Hooker Chemical Co.

Since manganese chloride had been of such vital im-

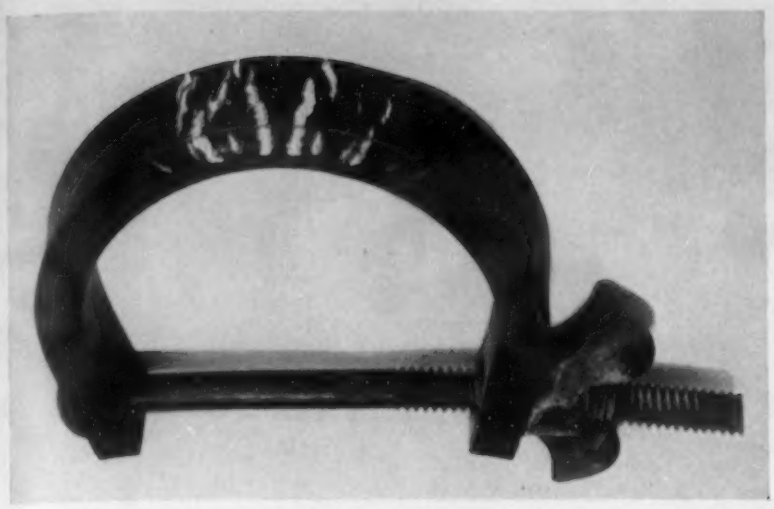


Fig. 10.—"U" Bend Specimen of Cold Rolled Steel Broken in Sodium Hydroxide-Sodium Nitrate Solution.

Solution	g./100 g. H_2O
NaOH	40
$NaNO_3$	0.2
$NaSiO_3$	0.2

portance in the action of the nitrate solutions it was added to the alkaline solutions in Table VI but cracking was not produced.

The solubility of manganous hydroxide in terms of the chloride in these boiling alkaline solutions is approximately as follows:

g.NaOH/100 g.H_2O	g.$MnCL_2$/100 g.H_2O
50	0.2
100	1.0

This would seem to be sufficient to exert some influence

Table VI.—Resistance of "U" Bend Specimens to Cracking in Boiling Sodium Hydroxide-Manganese Chloride Solutions.

Technical Sodium Hydroxide. g./100 g. H_2O				Specimens of Cold Rolled Steel.	
NaOH	$MnCl_2$	Na_2S	Na_2SiO_3		No Crack Days
25	0.1	..	..	.....	9
50	0.2	..	..	.....	9
50	1.0(*a*)	..	..	.....	9
50	0.2	0.2	..	.....	9
50	0.2	0.2	0.3	.....	9
100	1.0	..	..	.....	9
100	1.0	1.0	..	.....	9

(*a*) Amount added—this exceeds solubility.

if the manganese could produce the same action it does in the nitrate solutions.

The U-bend specimens were first cracked in seven days in sodium hydroxide solutions containing potassium permanganate. Table VII shows that the cracks could be produced in technical or chemically pure sodium hydroxide in a concentration of 50 grams per 100 grams of water in the presence of the permanganate. Increase in sodium silicate and increase or decrease in sodium hydroxide concentration tended to stop cracking.

The permanganate may have produced its influence either through oxidizing power or through the presence of the manganese. In the tests in Table VIII, sodium nitrate, a weak oxidizing agent was substituted for potassium permanganate, and intercrystalline cracking was readily produced in 3 to 7 days. High sodium silicate or appreciable quantities of manganous chloride tended to stop cracking. Fig. 9 shows that the cracks produced in the sodium hydroxide-sodium nitrate solution were 100 percent intercrystalline, and this was also true of the sodium hyproxide-potassium permanganate solutions.

During the tests the permanganate color disappeared,

Table VII.—Cracking of "U" Bend Specimens in Boiling Sodium Hydroxide Potassium Permanganate Solutions.

Technical Sodium Hydroxide. g./100 g. H_2O			Specimens of Cold Rolled Steel.		
NaOH	$KMnO_4$	Na_2SiO_3		Crack Days	No Crack Days
25	0.2	0.2	.....	..	7
50	0.2	..	.....	7	..
50(*a*)	0.2	..	.....	7	..
50	0.2	0.05(*b*)	.....	7	..
50	0.2	0.2	.....	7	..
50	0.2	0.2	.....	7	..
50	0.2	0.5	.....	..	7
100	0.2	0.2	.....	..	7

(*a*) Baker's chemically pure sodium hydroxide.
(*b*) Surface covered with very fine cracks.

probably indicating reduction to a manganic or manganous form. At the end of the nitrate tests, the solutions contained considerable amounts of both nitrate and nitrite.

The cracks in the boiler flange steel specimens developed mainly on the edge that was left covered with mill scale. This may indicate an intensification of stress or electrochemical attack due to the presence of the thick oxide coating.

Table IX shows that sodium nitrate concentrations from 0.2 to 1.0 gram per 100 grams of water were most effective

Table VIII.—Cracking of "U" Bend Specimens in Boiling Sodium Hydroxide-Sodium Nitrate Solutions.

Technical Sodium Hydroxide. g./100 g. H_2O				Specimens of Cold Rolled Steel.	
NaOH	$NaNO_3$	Na_2SiO_3	$MnCl_2$	Crack Days	No Crack Days
50	0.2	..	..	3	..
50	0.2(*a*)	..	..	8	..
50	0.2	0.2	..	7	..
50	0.2	0.2	..	6	..
50	0.5	0.2	..	3-7	..
50	0.2	0.5	..	..	7
40	0.02	0.2	>0.01	..	6
40	0.2	0.2	>0.01	4	..
50	0.2	0.2	0.01	..	7
50	0.2	0.2	0.1	..	7
100	0.2	0.4	..	..	7

(*a*) Specimens of boiler flange steel. Solution also contained 0.2 g. NaCl per 100 g. H_2O.

in causing cracking in 50 grams of sodium hydroxide per 100 grams of water. Three concentrations of sodium nitrate did not cause cracking in 25 grams of sodium hydroxide per 100 grams of water.

Fig. 10 shows the extensive cracking caused in the U-bend specimens by the sodium hydroxide-sodium nitrate solutions. . The position of the crack is outlined by the deposit of sodium carbonate resulting from the reaction of the sodium hydroxide, as it seeps out of the fissure, with the carbon dioxide of the air. Some of the fine cracks may also be seen.

Addition of other substances mainly unstable oxidizing agents such as sodium peroxide, sodium persulphate and sodium nitrite, to concentrated sodium hydroxide solutions did not produce cracking. A sodium hydroxide solution containing a small amount of sodium chromate did cause cracking.

The addition of a small amount of lead oxide (litharge) to the sodium hydroxide solutions has been found extremely effective in cracking the U-bend specimens. The results

Table IX.—Influence of Concentration on the Cracking of "U" Bend Specimens in Sodium Hydroxide-Sodium Nitrate Solutions.

Technical Sodium Hydroxide. g./100 g. H_2O				Specimens of Cold Rolled Steel.	
NaOH	$NaNO_3$	NaCl		Crack Days	No Crack Days
50	0.05	..	.....	..	7
50	0.2	..	.....	3	..
50	1.0	0.5	.....	5	..
50	5.0	..	.....	..	7
25	0.05	..	.....	..	7
25	0.2	..	.....	..	7
25	0.5	..	.....	..	7

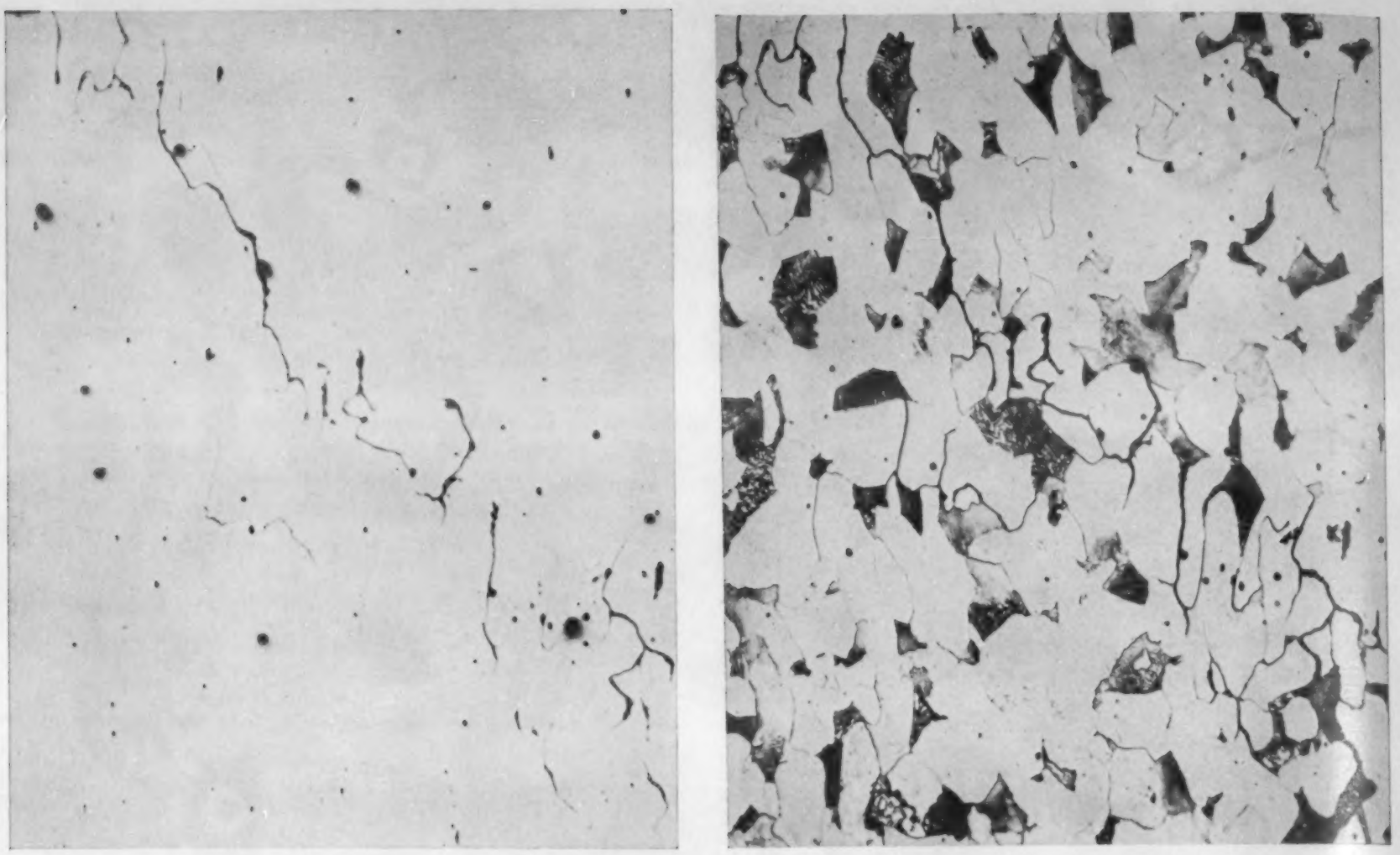


Fig. 11.—Intercrystalline Cracks Produced in a "U" Bend Specimen of Cold-Rolled Steel by a Nitric Acid-Manganese Chloride Solution.

Solution	g./100 g. H_2O
HNO_3	0.9
$MnCl_2$	0.05

Both are at a magnification of 500 X. The one at left was unetched and the other was etched with nital.

in Table X show cracking with the proper concentration of lead oxide in 50 and 100 grams of sodium hydroxide per 100 grams of water. These specimens were badly cracked in 1 to 2 days, whereas those in the sodium hydroxide-sodium nitrate solutions required 3 to 7 days. The sodium hydroxide-lead oxide solutions produce cracking almost as quickly as sodium nitrate-manganous chloride solutions, and in one respect are even more damaging since they penetrate the steel in many more places during the test.

Two specimens bent as shown in Fig. 4 but without the bolt and wing nut to create an applied load have been tested in sodium hydroxide-lead oxide solutions. Both specimens were cracked on the inside of the bend in much the same way as the specimen shown in Fig. 7. The radius of the bend as indicated by the figures, was much larger in these last two tests and after six days boiling the cracks had reached a depth of about 1/16 in. They extended down the legs to about an inch from the end of the specimen.

Table X.—Cracking of "U" Bend Specimens in Boiling Sodium Hydroxide-Lead Oxide Solutions.

Technical Sodium Hydroxide. g./100 g. H_2O			Specimens of Cold Rolled Steel.		
NaOH	NaCl	PbO		Crack Days	No Crack Days
25	0.2	0.2	.....	..	6
25	0.2	0.5	.....	..	7
50	0.2	0.005	.....	..	7
50	0.2	0.05	.....	..	7
50	0.2	0.2	.....	2	..
50	0.2	0.2	.....	2	..
50	0.2	0.2	.....	1	..
50	0.2	0.5	.....	6	..
100	0.2	1.0	.....	2	..

In a recent report by Berk and Schroeder[5] a theory was offered to explain the production of intercrystalline cracks. The mechanism involved covering the steel with a protective layer that was not sufficiently continuous to prevent the solution from attacking the grain boundaries. Such a coating might also be cathodic to the exposed or anodic grain boundaries and electrochemical action would accelerate the intercrystalline attack. In sodium hydroxide-sodium silicate solutions the silica has actually been found to deposit on the surface of the steel at 250 deg. C. A solution that will cause intercrystalline cracking at this temperature will not necessarily produce the same effect at some different temperature since either the sodium silicate may change its film forming characteristics or the corrosive attack of the sodium hydroxide may change.

Similarly the sodium hydroxide-sodium nitrate or other alkaline solutions that cause cracking while boiling at 124 deg. C. will not necessarily do so at 250 deg. C. This has actually been found to be the case, not only alkaline solutions but also the nitrate-manganese solutions fail to pro-

Table XI.—Cracking of "U" Bend Specimens in Hot Nitric Acid Solutions.

Temperature 70-80°C. g./100 g. H_2O		Specimens of Cold Rolled Steel	
HNO_3(a)	$MnCl_2$		Crack Days
0.9	0.05	.....	9
0.4	0.05	.....	9
0.2	0.02	.....	15
0.2	0.02	.....	12

(a) Concentration at start of test.

duce cracking of mild steel at the higher temperatures. In fact, from results previously reported[2] oxidizing agents such as nitrate in sufficient concentration have been found to prevent cracking of tension specimens in the sodium hydroxide-sodium silicate solutions at 250 deg. C. The difference in action of the nitrate at the two temperatures is most probably due to a change in the oxidizing power which it exerts on the steel surface.

At the atmospheric boiling point, only certain concentrations of nitrate in the sodium hydroxide will produce cracking, and increase in nitrate concentration with constant sodium hydroxide above a certain limit will stop this effect. This again may mean that the higher concentrations form a film which is too continuous to allow attack.

This explanation of the production of intercrystalline cracks on the basis of a non-continuous film seems to fit the observed facts quite well, but it should be subjected to amplification and modification with further experimental work. It also indicates that it may be possible to produce intercrystalline cracking with a pure solution such as sodium hydroxide, or sodium nitrate, if the concentration and temperature can be adjusted to maintain some corrosive action, and yet only partially cover the surface of the steel. Preliminary results now available, indicate that it is possible to do this at 150 deg. C. with sodium hydroxide. Such an adjustment would probably be quite critical and can be more easily attained by adding a second component to the solution and for that reason we find intercrystalline cracks occurring most frequently in a solution containing two substances.

Intercrystalline Cracking in Nitric Acid

If it is believed that intercrystalline cracking is produced by a corroding solution acting through a film which tends to cover the crystal faces, it should be possible to produce this type of failure under some conditions with an acid solution. Table XI shows that this can actually be done in very dilute nitric acid containing manganous chloride. Fig. 11 shows that the cracks resulting from these solutions are completely intercrystalline.

The tests were conducted with U-bend specimens in beakers covered with watch glasses on a hot plate at 70 to 80 deg. C. Loss of solution was made up by the addition of distilled water. Due to variation in test temperature, solution concentration, and oxygen taken up from the air, and added water, the results were not altogether reproducible. No difficulty was encountered, however, in obtaining cracks in at least one specimen in each series of tests.

The values in Table XI give the acid concentration at the start the test, the lowest values correspond to approximately 2000 parts per million of HNO_3. Due to the reaction with the steel specimen the concentration decreased during the test, usually reaching a pH value from 3 to 5 at the end. Visual observation would lead to the belief that most of the cracking occurred during the last part of the test, when the acid concentration was very low.

These experiments led to some very interesting possibilities. If intercrystalline cracking can be produced in a solution with a pH somewhat below 7, could it possibly be produced in a solution whose pH is between 8 and 13? The alkaline solution is less corrosive than the acid but the sodium nitrate-manganese chloride mixtures that so rapidly cracked the steel did not cause visible surface attack at all. As yet there is no indication that a solution must produce general surface corrosion to cause intercrystalline cracking. The failure of laboratory experimentation to produce this cracking in a dilute alkaline solution may be due to the lack of understanding that has existed to the present time concerning the possible influence of small amounts of other substances. The action of the dilute solutions is being investigated at the present time.

This question is of prime importance in cracking of boiler steel since it has always been believed that several hundred-fold concentration of the boiler water must take place in the seams before intercrystalline attack occurs. If this is not true or if only a few fold concentration is necessary, the basis for treatment to prevent cracking must be revised.

Conclusions

Tension tests and U-bend tests indicate that concentrations and temperatures must be carefully adjusted to produce intercrystalline cracking. For example, sodium hydroxide-sodium silicate solutions produce failure of tension specimens at 250 deg. C., but have not yet produced cracking of U-bend specimens at the atmospheric boiling point. On the other hand, the presence of small amounts of potassium permanganate, sodium nitrate, or sodium chromate will cause cracking of the U-bend specimens in sodium hydroxide solutions boiling at atmospheric pressure, but these same substances in the correct concentrations will protect the steel against the action of sodium hydroxide-sodium silicate solutions in the tension tests at 250 deg. C.

The experimental results suggest that intercrystalline cracking is produced by a solution that tends to form a protective film over the crystal surfaces while it attacks the grain boundaries. This condition can most easily be attained with two dissolved components, but with careful adjustment it may be possible to produce cracking in a solution containing only one dissolved substance. The intercrystalline corrosion may be accelerated by electrochemical potentials existing between the protected crystal faces and the grain boundaries as well as by the presence of hydrogen depolarizers. Progress of the crack may be enhanced by bursting forces existing within the grain boundaries if the corrosion products occupy a greater volume than the iron itself. From this suggested mechanism it has been possible to predict and prove that very dilute nitric acid solutions could be substituted for sodium hydroxide solutions to produce intercrystalline cracks.

These new results and their explanation have broad and important implications with respect to the production of intercrystalline cracks in boilers.

First, not only one solution but a variety of solutions of different compositions may promote failure. To be destructive it seems necessary that the solution produce a non-continuous film on the steel and corrode the grain boundaries.

Second, since the reactions may be started or stopped by surface conditions on the steel, they will obviously be extremely sensitive to small changes. For example, a boiler operating with low dissolved oxygen may not encounter trouble until the concentration is allowed to increase and possibly form a film that will promote intercrystalline attack. On the other hand, if the oxygen increases still further, the attack may be stopped. Oxygen has merely

been used as an example; salts such as nitrate, silicate, etc., play an important part. This sensitivity to changes in conditions gives the study somewhat the complexity of the corrosion problem and indeed in a number of aspects similarities are indicated.

Third, since temperature and solution conditions must be quite accurately adjusted to produce cracking, it may occur only intermittently in a boiler. If this is true water taken from a boiler after cracking has been found will not necessarily indicate the correct conditions to produce intercrystalline failure.

Fourth, some substances that are used to prevent cracking do so by changing or producing a new surface film on the steel. Under certain conditions effective protection exists, yet the very formation of a film may promote intercrystalline cracking if the conditions are changed.

Fifth, the results definitely show that it is not necessary to have an applied load on the steel to produce cracking. The internal stresses resulting from cold work or other treatment will allow the solutions to attack the steel. If an applied load is present it may of course hasten ultimate failure and at the same time give cracks that are partly intercrystalline and partly transcrystalline. Sixth, neither repeated stress nor corrosion fatigue necessarily play a part in the production of this type of cracking. They also may hasten the destruction of the metal but cracking can be produced in their entire absence.

In this discussion no definite reference has been made to the influence of steel composition on failure because it has not yet been subjected to systematic investigation. As an incidental part of the study, certain steels have been found to be more readily cracked than others. For instance, a series of $\frac{5}{8}$ in. bolts used in some of the tests were so badly attacked on the unthreaded portion that they could readily be broken into disks or wafers with a light tap of the hammer. The specimens in these same solutions developed only very small cracks. The malleable cast iron nuts used on the U-bend specimens, as in Fig. 4, were very easily attacked. Free machining stainless steel is probably more susceptible to the action of some of the solutions than any other material which has been used. The rate, or degree of attack, seems to vary from steel to steel, but intercrystalline cracks have been produced under certain conditions in all the materials that have been tested, including Armco ingot iron and non-aging steel.

As a result of this broadened viewpoint concerning the production of intercrystalline cracking it may appear that the development and study of satisfactory protective agents will become very complex. Certain simplifications can, however, be made. If a protective agent is found to be satisfactory in several solutions which cause rapid cracking at different temperatures, it seems reasonable to conclude that it should offer protection in almost every case encountered in operation.

Investigation is being made on the action of possible protective agents at the present time as well as a study of the action of dilute alkaline solutions in producing intercrystalline cracking.

Acknowledgements

The authors wish to acknowledge the assistance of J. R. Villela, and J. O. Light of the United States Steel Corp. in the preparation of the photomicrographs in this paper, the constructive review of the manuscript by Everett P. Partridge of Hall Laboratories, Inc., Pittsburgh, and the kindness of Subcommittee No. 6 of the Joint Research Committee on Boiler Feedwater Studies in granting permission for publication.

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BRIGHT ANNEALING OF

Seamless Steel Aircraft Tubing

by H. R. Lewis

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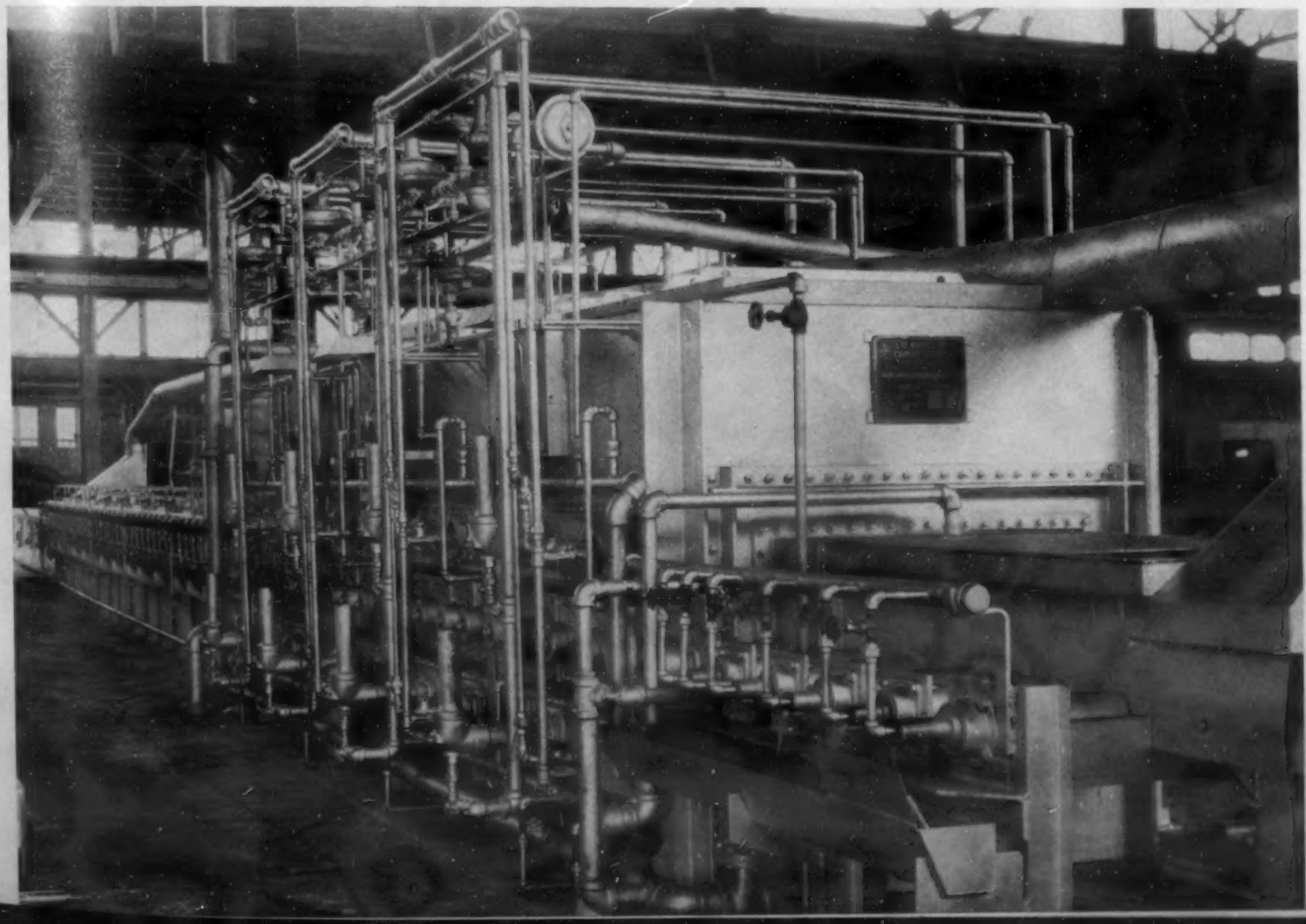
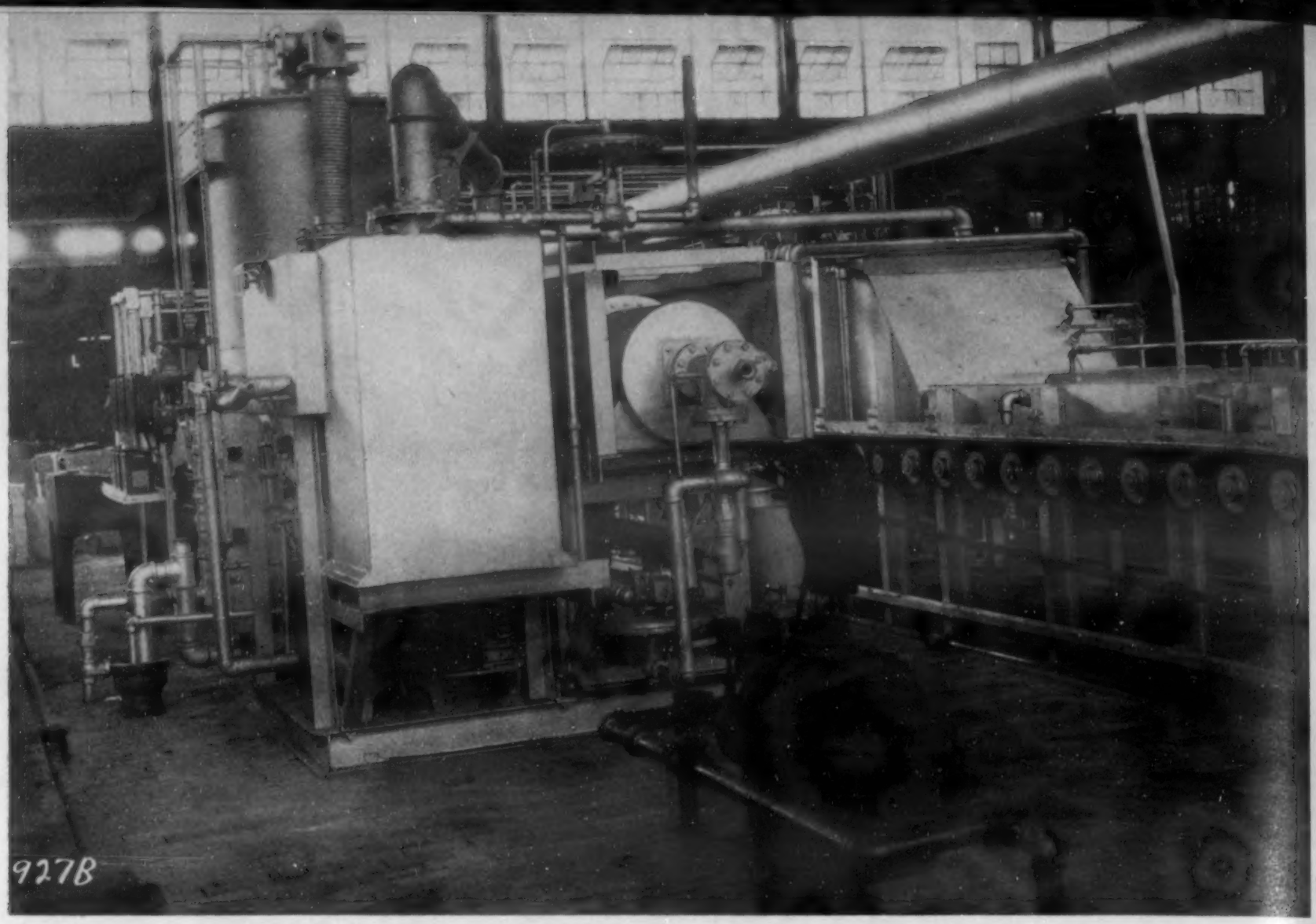
THE HIGH STANDARDS of both material and workmanship required and maintained in the aircraft industry are well known. In the construction of the fuselage, for instance, seamless steel tubing is used. The processing of this tubing, especially the heat treating, must be very precise in order that the finished product conform with the stringent specifications of hardness, grain size, and carbon content.

In the processing of this tubing it is common practice to hot pierce a billet and to perform all subsequent drawing operations cold. In some instances, as many as six or more cold drawing operations are necessary to reduce the pierced billet to the desired size tubing. It is the A, B, C's of metallurgy that cold working hardens the metal. Consequently, after each drawing operation, the tubing must be annealed before additional drawing.

Seamless steel aircraft tubing usually has a medium carbon content, S.A.E. 4130 (carbon content 0.25 to 0.35%)

View Taken from Charge End Showing Water Cooled Bearings and Mounting of the Gas-Fired Radiant Heating Elements.

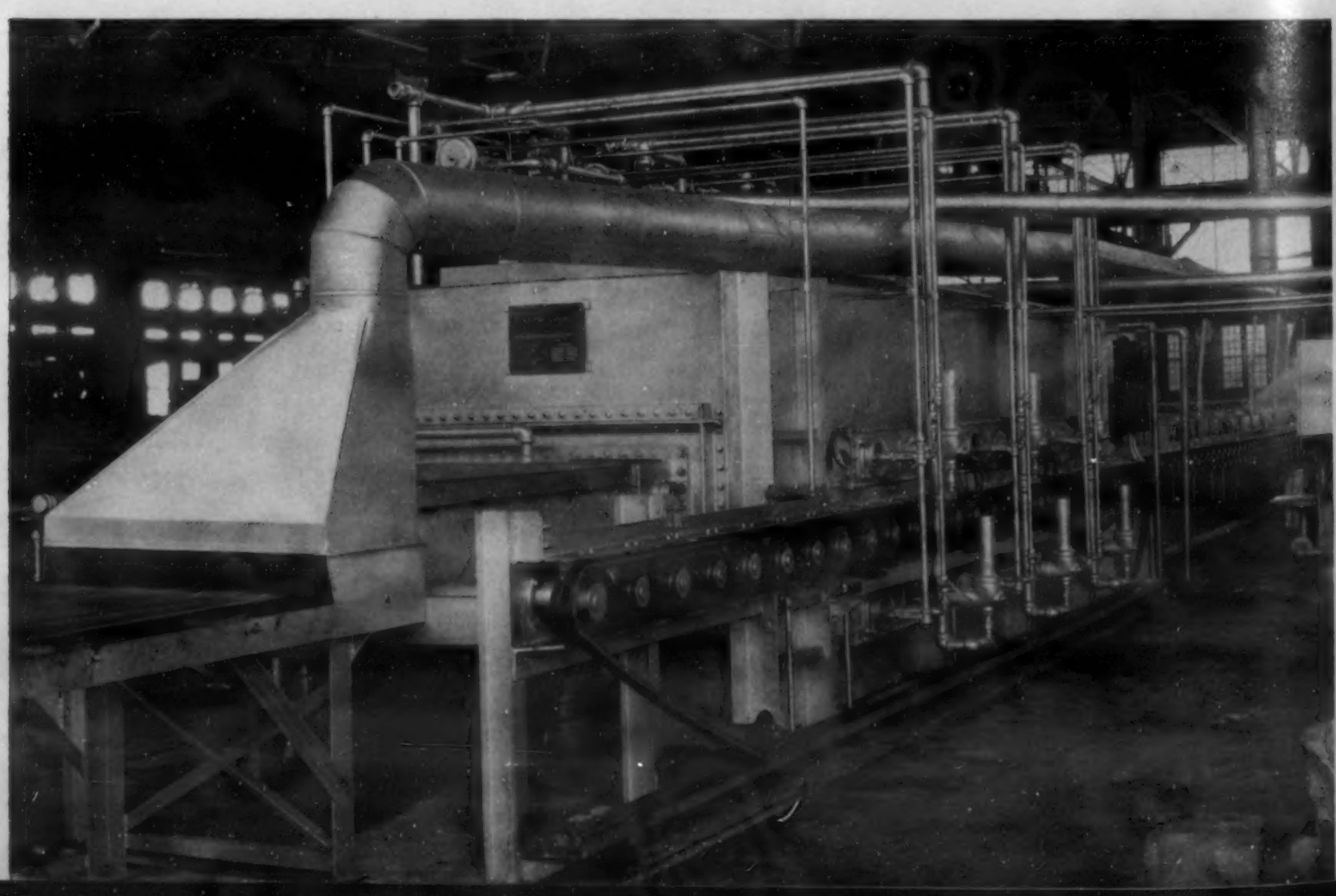


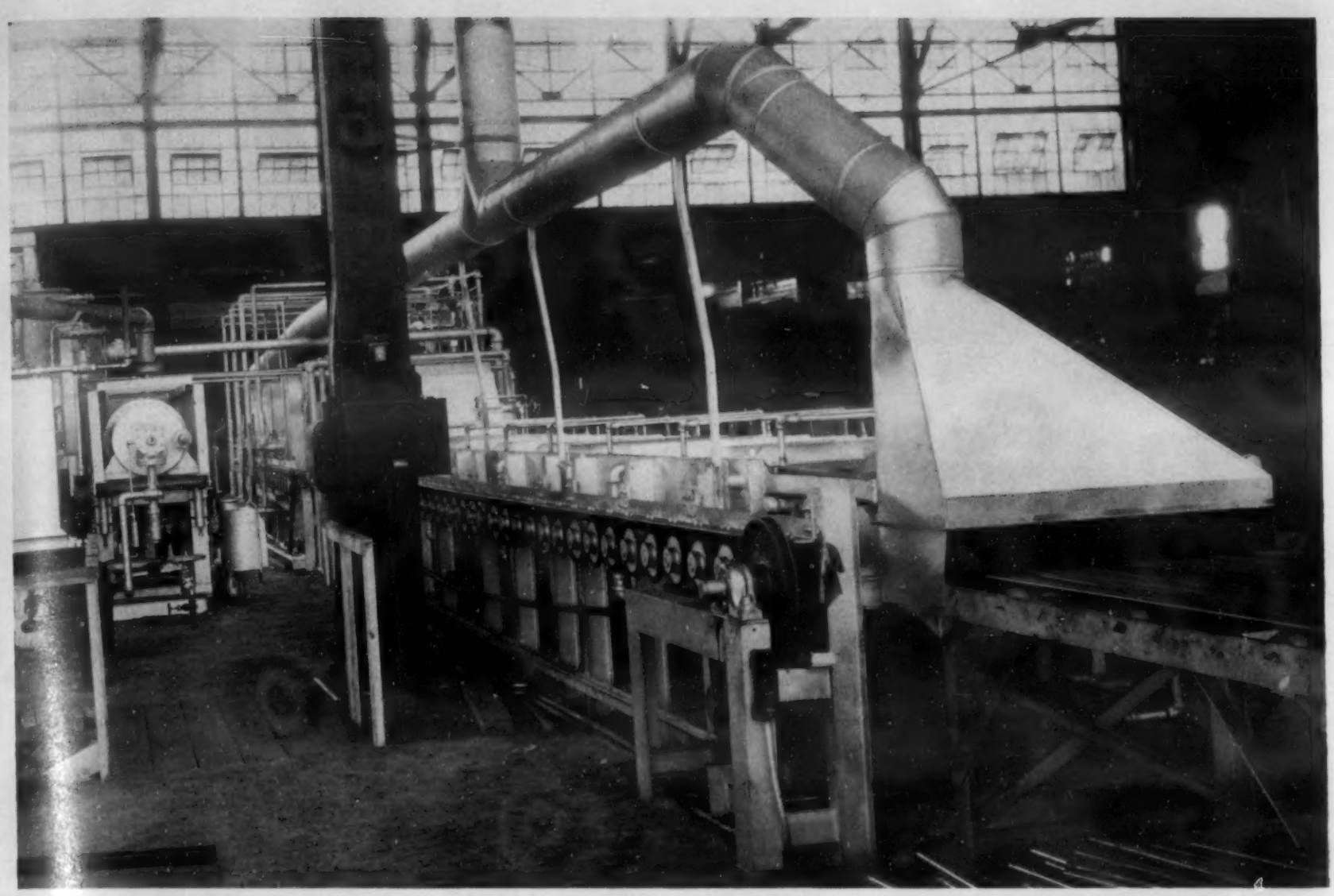


View of DX Atmosphere Gas Preparation Machine with Discharge End of Furnace in Background.

being commonly used. It has long been a problem to anneal such tubing without decarburization and to eliminate the danger of acid embrittleness resulting from overpickling. The Ohio Seamless Tube Co. of Shelby, Ohio, recently installed a continuous controlled atmosphere furnace which is satisfactorily meeting the problem of decarburization and which has eliminated the danger of acid embrittlement since only a flash pickle is required on the process anneal. It has been found that a flash pickle is desirable on the process annealed work as this pickle pro-

View Taken from Charge End Showing Method of Driving Roller Conveyor. Six Burners and Eductors Mounted on Ends of Gas-Fired Radiant Tube Heating Elements Are Also Shown.





View Taken from Discharge End of Furnace Showing Tubes Leaving Cooling Chamber.

duces a surface to which the drawing compound adheres better than on a more smooth surface. The final or finished annealed tubing is not pickled.

The furnace is of gas-fired radiant tube type, the heating chamber having internal dimensions of 3 ft. 6 in. by 17 ft. 0 in. The over-all length including charge table, eductor, cooling chamber and discharge table is approximately 150 ft. The rated capacity is 2000 lbs. per hr. of finish annealed tubing and 3000 lbs. per hr. of processed annealed tubing.

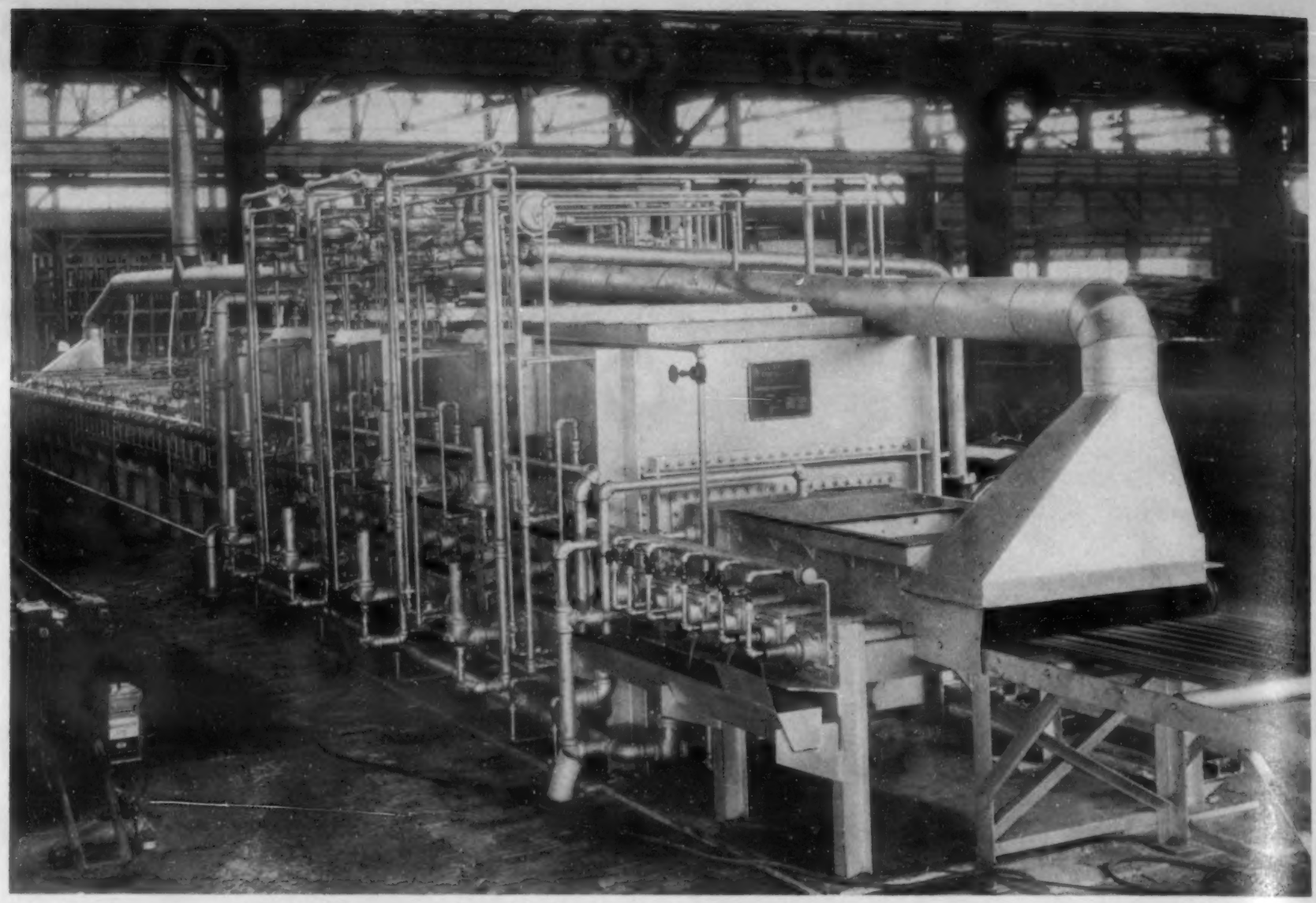
The radiant tube heating elements are mounted through the side walls, both above and below the conveyor. There is a total of 16 heating elements, each being made of an alloy tube having the general outline of the letter "W" and positioned horizontally across the width of the furnace chamber. Since each tube has four legs, there are in reality 64 cross tubes in the furnace. Each of the 16 heating elements is provided with a special combination premix and diffusion type burner. The tubes when in operation are under a gentle suction produced by means of an eductor at the discharge end of the tube. This gentle suction makes it impossible for the products of combustion to escape from the tubes even though a leak or crack does develop. Hence, repairs to the tubes, if needed, can be postponed until production permits as the suction makes it impossible for the products of combustion to escape into the furnace and contaminate the special furnace atmosphere which is maintained in both the heating and cooling zones.

The tubes are conveyed through the furnace continuously by means of power driven rollers. In the heating zone, these rollers are cast of heat-resisting alloy and are mounted through the side walls in water cooled bearings of the self-aligning type. In the cooling chamber, the first three rollers are also made of heat-resisting alloy, the remainder being of steel. All rollers in both the heating and cooling zones are equipped with a sprocket at one end. The sprockets are driven by means of a chain which extends the full length and along one side of the furnace and cooling chamber.

In order to cool the work in a protective atmosphere and at the same time provide a means of regulating the rate of cooling, there is located at the discharge end of the furnace a cooling chamber. This is a continuation of the furnace but is separated from the furnace proper by an internal door which may be regulated to suit different sizes of tubing. Substantially constructed of structural steel plates and shapes, this chamber is made up in a plurality of individual sections. Each section is provided with a water jacket on the sides, top and bottom. In addition, the first section next to the heating chamber is equipped with a vertical type circulating fan mounted through the roof. The purpose of this fan is to permit changing the cooling rate of the work passing through the cooling chamber.

Playing an essential part in the operation of this furnace is the special protective atmosphere maintained in both the heating and cooling chambers. It is this atmosphere which prevents decarburization and oxidation and thus does away with the necessity of heavy pickling. The tubes leave the furnace with a bright finish and, after the finish anneal, are either stored or packed for shipment without an additional processing operation.

Of much more importance than oxidation, however, is



View also Taken from Charge End Showing Tubes Entering the Furnace.

the ability of this furnace to anneal without decarburization. Tests have shown a piece of SAE 4150 tubing to be annealed as many as 8 times without decarburization. Additional tests for temperature distribution showed a maximum variation of only 5 deg. F. across the hearth of the furnace at 1400 deg. F.

Regarding the decarburization of S. A. E. steel 4150 tubing, the tests for decarburization were made by determining the total carbon content of the steel before and after annealing. After piercing the 4150 steel, the carbon content was found to be 0.518 to 0.536 per cent. After eight anneals its total carbon was found to be 0.518 per cent. The furnace was guaranteed not to decarburize steel tubing with a carbon content up to 0.35 to 0.40 per cent. Since these tests were made chemically, no photomicrographs are available for presentation.

The drawing temperature in the furnace is 900 to 1000 deg. F., the annealing temperature is 1400 deg. F. and the normalizing temperature is 1650 to 1725 deg. F. The variation in temperature is accounted for by the different steels used. The time the work is in the heating chamber varies from 4 mins. to 64 mins. depending on the size of the tubing. The conveyor has a 16 to 1 speed ratio, made possible by a 2-speed motor (950 and 450 r.p.m.) and an 8 to 1 variable speed transmission. The length of the tubing varies from a minimum of 5 ft. to a maximum of 37 ft.

The atmospheric gas, known as DX gas, is manufactured in the unit separate from the furnace. Suitable portions of air and gas are cracked or partly burned in a horizontal refractory lined combustion chamber which is at a relatively high temperature. After leaving the combustion chamber, the cracked gas passes through a series of towers where it is scrubbed and dropped to approximately tap water temperature. It then passes to a refrigerator where additional dehydration takes place. After leaving the refrigerator, the atmospheric gas then passes through a heating chamber and then on to the furnace proper. This reheating has a catalytic effect which tends to stabilize the gas which in turn is claimed to be much more effective in preventing decarburization.

The dew point of the dehydrated DX gas is 38 deg. F. The air-gas ratio of the DX gas is approximately 6 to 1, using natural gas.

The furnace is in production 24 hrs. a day, six days and, at times, seven days a week. During the week the furnace is normally used for process annealing. On Friday or Saturday, the furnace temperature is raised to normalizing temperature only to be cut back to 900 deg. F. on Sunday so as to have the furnace ready for bright drawing on Monday morning.

Regardless of the type of heat-treating operation, the furnace is performing equally well both as regards bright surface and metallurgical requirements. The temperature distribution from side to side of the furnace is very uniform, and, consequently, the hardness of the work is within a range of two points Rockwell. The furnace was designed, fabricated and installed by the Surface Combustion Corp. of Toledo, Ohio.

The Pitting of Stainless Steel

AND THE INSOLUBILITY OF FERRIC ION IN SEA WATER

by W. A. Wesley and C. H. Lindsley

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PROGRESS IN UNDERSTANDING the mechanisms by which pits are initiated in passive surfaces will be delayed by general acceptance of any explanation which involves an unsound assumption. It is well known that an acidified solution of ferric chloride can be applied to stainless steels to produce a rapid, sharply localized form of corrosion. This to some extent simulates the effects of the slower attack sometimes observed when such steels are exposed in slowly moving sea water, and the ferric chloride solutions are indeed useful in laboratory investigations of the causes of such pitting.[1]

Little has appeared in print on this subject, but it is being discussed actively among those interested in corrosion and the belief has spread that the pits are started by the action of iron salts in sea water. It should be noted that the chief mystery which surrounds this phenomenon is not why the corrosion progresses after pits start but what it is that starts them.

Proponents of the idea that iron salts in sea water initiate pits fail to take account of the fact that ferric iron is insoluble in sea water at a pH above 3. The hydrogen ion concentration of natural sea water from the Atlantic Ocean[2] lies between pH 8.1 and 8.3. The work described in this report shows that the solubility of ferric ion in sea water is less than one part per million at hydrogen ion concentrations of pH greater than 3.

Solubility Measurements

The method used in determining the solubility of ferric iron was to prepare a saturated solution of ferric chloride in synthetic sea water at pH about 1.5, then adjust the pH to a desired higher value by addition of a solution of sodium hydroxide, boil to coagulate any colloidal ferric hydroxide formed, filter, and then determine accurately the hydrogen ion concentration and iron content of the filtrate.

An artificial sea water was made in accordance with the U. S. Navy specification No. 47 S 20 as used in salt spray testing. Its composition is as follows:

Stock Solution:	
Potassium chloride	10 grams
Potassium bromide	4.5 grams
Magnesium chloride, hexahydrate	550 grams
Calcium chloride, hexahydrate	110 grams
Distilled water to make one liter	
Artificial Sea Water:	
Sodium chloride	23 grams
Sodium sulphate, decahydrate	8 grams
Stock solution	20 cu. cm.
Distilled water to make one liter	

At the outset it was realized that the principal difficulty would be met in keeping excess iron from going into colloidal solution as ferric hydrosol. The procedure finally adopted was the following:

About 1.5 grams of ferric chloride were dissolved in one liter of sea water. This was heated to boiling under a reflux condenser. The precipitate that formed was dissolved by the addition of small amounts of concentrated hydrochloric acid, and then the excess hydrochloric acid was neutralized by small additions of 10-normal sodium hydroxide until a permanent precipitate was formed. Boiling was continued for a minute or so to ensure complete precipitation, and the mixture was filtered while hot. The resulting clear yellow solution had a pH value of about 1.5 and contained nearly one gram of ferric chloride per liter. To portions of this solution were added various amounts of 1-normal sodium hydroxide (made up with 23 grams sodium chloride and 8 grams sodium sulphate decahydrate per liter). Each portion was boiled for a short time to coagulate the colloidal ferric hydroxide. The precipitate was then filtered off, and the hydrogen ion concentration and iron content of the filtrate were determined.

The pH values were measured with a standardized commercial glass electrode apparatus.

The iron concentration was determined colorimetrically

with ammonium thiocyanate. As ordinarily recommended in reference books on analytical chemistry, this analysis is carried out in dilute sulphuric acid, and chlorides of the alkaline-earth metals (including calcium and magnesium) interfere with the development and stability of the color. The method for converting the chlorides to sulphates is rather tedious, especially in view of the rather large number of determinations to be made. It was found, however, that these difficulties could be overcome by carrying out the analysis in HCl instead of H_2SO_4. The reliability of this altered procedure was checked by actually determining colorimetrically the amount of iron in a solution of acidified sea water and comparing with determinations by titration with standard potassium permanganate solution.

The iron concentrations at various pH values are given in the Table and are shown graphically in the illustration.

Table of Iron Concentrations at Various pH Values

pH	Iron concentration, p.p.m.	pH	Iron concentration, p.p.m.
1.46	340	1.98	31.5
1.59	200	1.99	20.
1.61	160	2.05	4.
1.64	275	2.20	17.5
1.65	100	2.20	0.2
1.67	190	2.22	9.5
1.67	100	2.30	4.
1.70	49	2.93	1.4
1.73	58.5	6.1	0.1
1.78	48	10.2	0.0
1.85	48	...	...

The irregularity at the lower pH values may be explained by the marked effect on the solubility produced by a very slight change in pH. This is made clear by a consideration of the illustration.

It must be emphasized that the iron concentrations recorded are probably too high rather than too low. Ferric hydroxide, which is the precipitate formed, has a strong tendency to pass into the colloidal state and so be included in the estimation of iron. A few supplementary tests showed that at pH 8 or 9, however, even this source of error could be neglected. No iron could be detected in the synthetic sea water solution at pH 8.0 or 9.0 even after it was agitated in contact with freshly precipitated ferric hydroxide overnight and filtered.

Solubility Product

The following equation is an exact expression of the solubility product principle of Noyes:

$$a_{Fe^{+++}} \cdot (a_{OH^-})^3 = K \qquad (1)$$

In the experimental work the actual quantities measured were the activity of hydrogen ions and the stoichiometric concentration of ferric iron in solution. On the assumption that the dissociation constant of water K_w is constant with variation in pH of the sea water solution, the activity of hydroxyl ion needed in equation (1) can be readily computed from the relation

$$a_{OH^-} \cdot a_{H^+} = K_w = 10^{-14} \qquad (2)$$

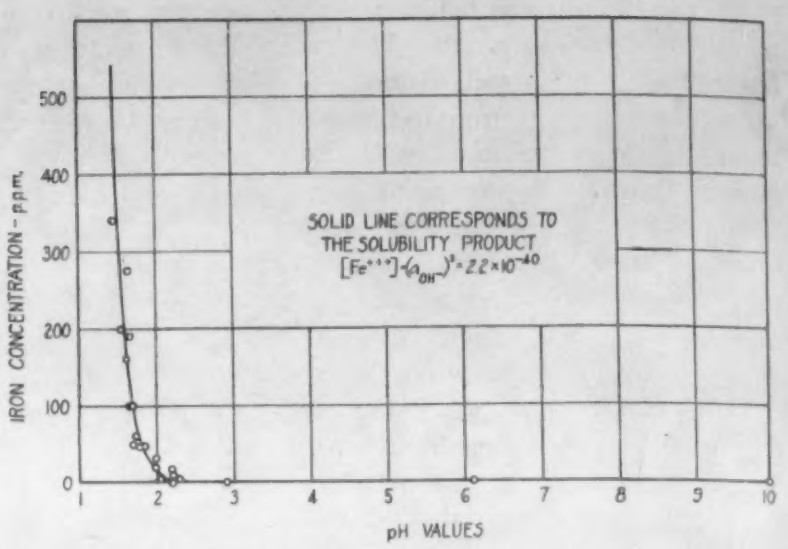
Since

$$a_{Fe^{+++}} = \gamma_{Fe^{+++}} \cdot [Fe^{+++}] \qquad (3)$$

where $[Fe^{+++}]$ is the stoichiometric concentration of ferric iron and γFe^{+++} is the activity coefficient of the ferric ion, equation (1) becomes

$$\gamma_{Fe^{+++}} \cdot [Fe^{+++}] \cdot (a_{OH^-})^3 = K \qquad (4)$$

Now the ionic strength of the sea water solution does not change much with change in pH from 1 to 10. This makes it reasonable to assume that the activity coefficient,



Solubility of the Ferric Ion in Artificial Sea Water

γFe^{+++}, of the ferric ion does not change with such change in pH in this solution. If γFe^{+++} is constant, then equation (4) becomes identical with the solubility product equation ordinarily used for ferric hydroxide, namely,

$$S = [Fe^{+++}] \cdot (a_{OH^-})^3 \qquad (5)$$

The curve of the illustration represents equation (5) when $S = 2.2 \times 10^{-40}$. The experimentally determined points agree well with this curve.

It is interesting to compare this value of S with the following quoted by Mellor in his "Treatise on Inorganic Chemistry," vol. XIII, p. 894:

Bodländer	6.5×10^{-47}
Jellnick and Gordan	$1 \times 10^{-37.0}$
Ruff and Hirsch	1×10^{-36}
Müller	6.5×10^{-47}
Britton	$1 \times 10^{-37.7}$

Iron in Natural Sea Water

Iron has been reported in analyses of natural sea waters as in the Mediterranean Sea (3 p.p.m.), Caspian Sea (40 p.p.m.) and Black Sea (127 p.p.m.)[3] but Harvey, in his classic "Chemistry and Physics of Sea Water" states that sea water gives no reaction for ferric iron unless the organic compounds are destroyed by drastic oxidizing treatment. He states that the minute amount of iron present in sea water is probably there in the form of organic matter. In this form the iron would not take part in the relationship upon which the solubility product is based and presumably would not behave like the ferric ion in initiating local corrosion.

Pitting of Stainless Steel

The experimental results indicate that the solubility of the ferric ion at the pH of natural sea water is less than one part in ten million and is less than one part per million even at a pH as low as 3. For ferrous salts, however, the story is different. Assuming that the solubility product of ferrous hydroxide is of the order of 10^{-15} the estimated solubility of ferrous iron at pH 8 is only 60 parts per million, but this becomes appreciable even at pH 7 where the estimate would be 6000 parts per million.

If stainless steel is observed to corrode in a sea water application and some source of iron compounds, such as corroding iron or steel, is identified in the vicinity, then it is still necessary to prove the operation of one of the

following mechanisms before fixing blame upon the action of dissolved iron salts: (1) The pH of the sea water was lowered from 8 to well below 3.0, thus overcoming the insolubility of ferric iron and permitting the accumulation of appreciable concentrations of dissolved ferric chloride; (2) The pH was lowered to below 7 and oxidation of ferrous salts was prevented before their arrival at the surface of the stainless steel. In this case it would also be necessary to prove that solutions of ferrous chloride can cause pitting of the type observed.

The first mechanism is not plausible because no process has been suggested by which the pH could have been lowered so much in any reported instance of pitting of stainless steel in sea water. The second mechanism is still open to support. Under special conditions it does seem possible that ferrous chloride initiates pitting. The observation has frequently been made by members of this department in examining stainless steel specimens exposed in natural sea waters on the Atlantic Coast that there is a tendency for pitting, once it has started, to progress vertically downward.

It has been customary to ascribe this to the shielding action of the solid ferric hydroxide generated at the pit and settling upon the surface of the steel in a streak below. Perhaps the truth is that some of the ferrous chloride solution formed at anodic regions within the pit was able to escape oxidation and precipitation momentarily as it oozed out of the pit and along the surface. Whether or not such a solution would attack stainless steel remains to be learned. In any event, it is not probable that appreciable amounts of ferrous chloride formed at anodic areas of corroding iron or steel could diffuse or be carried very far through sea water without neutralization by the alkali formed at cathodic areas, and without oxidation and consequent precipitation as ferric hydroxide. Attempts failed to detect ferrous ions in tanks of neutral aerated salt water in which large pieces of steel were corroding with copious formation of ferric hydroxide. The pH in such tanks tends to reach equilibrium at a value between 6 and 7.

Conclusions

The insolubility of the ferric ion in sea water at pH 3.0 or higher makes vulnerable any theory that pitting of stainless steel in sea water applications is initiated by ferric chloride generated by corroding iron or steel in the vicinity.

Although ferrous chloride is soluble below pH 7, it is readily oxidized and precipitated as ferric hydroxide by the action of dissolved air. It does not seem probable that this salt is a common cause of pitting.

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[2] Harvey. "Chemistry and Physics of Sea Water," 1928, p. 72.
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A LETTER TO THE EDITOR

Transformation Mechanisms and Tensile Stress in Fe-Ni Alloys

To the Editor: Günther Wassermann has reported some interesting experiments on the influence of an applied tensile stress upon the γ-α transformation in Fe-Ni alloys containing 30 per cent Ni (*Archiv Eisenhüttenwesen,* Vol. 10, pages 321-5, 1936 to 1937; Vol. 11, pages 89-92, 1937).

The material used was a sheet containing a cubic recrystallization texture, i.e., a pseudo single crystal. When the unstressed sample was transformed in liquid air, the areas of α needles defined directions $\pm$ 17 deg. to the rolling direction of the sheet. If a tensile stress was applied parallel to a cube direction, also the rolling direction, with increasing stress the $\pm$ 17 deg. pattern disappeared in favor of a pattern $\pm$ 56 deg. to the rolling direction. By cutting the sheet so that the tensile direction was 45 deg. to the cube direction, the pattern was again shifted so that the defined directions were $\pm$ 25 deg. to the cube axis and the rolling direction. The imperfection of the cubic structure made accurate study of the orientation relations impossible, but the information obtained indicated that the usual (111)γ // (110)α relation existed. The X-ray work also demonstrated that, upon reversing the transformation by annealing at 500 deg. C., the original cubic γ texture reappeared in spite of the considerable deformation of the specimen. Wassermann proposes that these experiments indicate that tensile stress changes the crystallographic mechanism of the transformation.

This conclusion may very well be correct, for recent work indicates that transformation mechanisms are dependent upon the type of crystallographic shear which may occur under the conditions of the experiment, and two different mechanisms have been demonstrated in Fe-Ni alloys of this composition (A.I.M.E. Tech. Pub. 797, 1937). However, I do not think that Wassermann's experiments establish his point. He states, and his micrographs show, that the directions referred to are not those of individual needles, but rather of conglomerates. The directions defined by these conglomerates are apparently determined by areas of high stress in the original γ sheet; nucleation of the α phase is therefore more rapid in these regions, and the transformation is more complete there. The existence of Lüders' lines and strain figures in low carbon steels is evidence that such strain patterns form, and the variation of these patterns with the direction of tensile stress has been shown (summarized, *Trans.* A.S.M., Dec. 1936, pages 1022-3).

Studies by Köster (Archiv. Eisenhüttenwesen, Vol. 3, 1930, 653) on the influence of deformation on nitride formation in steels have shown that a large number of nitride needles may form along a slip line, giving the appearance of a pattern determined by the slip line. However, at higher magnification it is seen that the individual needles have taken other directions which correspond to those directions normally chosen in unstrained material. The same phenomena have been observed in relation to twins. (These observations are discussed in greater detail in A.I.M.E. Tech. Pub. No. 820, 1937). Widmanstätten studies have also demonstrated that the crystallographic mechanisms of solid transformations are independent of the outward form of the precipitate, and that they are even unchanged when the precipitate forms no definite Widmanstätten pattern. (See especially II and VII of the *Studies upon the Widmanstätten Structure,* appearing in A.I.M.E., 1931 to 1937.) In consideration of this evidence it would seem that a complete crystallographic study of transformations under stress will have to be made before Wassermann's conclusion can be accepted.

The retention of the original cubic texture after the transformation cycle, in spite of permanent deformation, is readily understood. The X-ray photograms and micrographs both show that the transformation to α has never been complete. The untransformed γ therefore nucleates the reverse transformation so effectively that no new nuclei of different orientation can appear.

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Courtesy: Ford Motor Co.

Taking the Temperature of Liquid Steel with Optical Pyrometer

THE TEMPERATURE OF Recrystallization of Nickel

by Erich Fetz

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This article presents another phase of the author's extended study of the recovery of cold-worked nickel on annealing. In other publications,[1,2,3] he has investigated the release of hardness and tensile strength of cold-worked, highly pure nickel; in the present separate yet related work, he locates the temperature range in which the deformation structure, as seen under the microscope, is abolished. The results reported below are of interest not only because knowledge of the recrystallization temperature of a metal is a decidedly practical asset, but because the unusually low recrystallization temperature found by the author adds another scientific bit to our revised understanding of the properties of highly pure metals.—Editors.

THE RELATION BETWEEN RELIEF of work hardening and microscopic recrystallization (particularly grain size and grain growth) is a subject not only of theoretical, but of considerable practical importance. For example, in certain shaping processes, like deep drawing and stamping, the size and arrangement of the recrystallized grains profoundly affect the behavior of the material in a manner and to a degree not predictable from information on its strength or hardness. Grain size and arrangement of grains are vital factors in the performance of thin wires exposed to high temperatures. Thus, tungsten filaments consisting of one or a very few long grains are superior to fine-crystalline wire, and the recrystallization of tungsten has even been so controlled that the grain boundaries can be made to approach the wire surface at an acute angle; the length of a crystal, therefore, may be several times the diameter of the wire.[4] Ransley and Smithells[5] have demonstrated the effect of the relative dimensions of the grains and the wire itself on the tensile properties of fine nickel wires. Hessenbruch and Rohn[6] found that the life of a fine-grained nickel-chromium resistor wire at high temperatures was longer by 40 per cent than that of a coarse-grained sample drawn from the same melt.

The presence of impurities also exerts a notable effect on grain growth. If the impurity is an insoluble non-metallic inclusion (like thoria in tungsten filament) it may restrict grain growth by acting as a nucleus in initiating the formation of a large number of grains during primary crystallization; impurities held in solid solution, however, frequently have an opposite effect. Tests on two brands of aluminum of 99.2 and 99.9 per cent purity showed that, with the same amount of plastic deformation, materially higher temperatures were necessary to produce a coarse-grained recrystallization texture in the less pure grade.[7]

Earlier Studies on Nickel

A review of existing statements in the literature on the recrystallization temperature of nickel reveals as much general confusion as prevailed concerning the temperature range of hardness recovery. Furthermore, the findings on the relative location of the temperature range in which work hardening is released and that in which the deformation structure is abolished, are also in disagreement. It appears to be advisable, therefore, not only to re-attack the problem of the recrystallization temperature of high-purity nickel, but also, using different kinds of nickel, to answer once and for all the question of its location relative to the temperature at which hardness recovers. We may ask, for example:

(a) does hardness recover only after complete recrystallization, as claimed by Dreyer and Tammann[8], or

(b) do softening and recrystallization occur simultaneously, as is generally held, or finally

(c) is a new grain structure formed after most of the work hardening has been released, as has been established beyond any doubt with tungsten, aluminum, and aluminum alloys?

Price and Davidson[9] present microstructures at 75X of cold-rolled nickel (98.48 per cent Ni + Co) annealed at different temperatures for 20 mins. after being heated to temperatures in 25 mins. (unusually slowly). No visible recrystallization at 75X is noticed until a temperature of 650 deg. C. is reached; at 750 deg. C. complete recrystallization takes place. One-half of the work hardening is lost at $T_r = 620$ deg. C. [Note: T_r, the recovery temperature, has previously been defined[1] as the temperature at which the curve of hardness vs. annealing temperature reverses its convexity. In most cases this corresponds to the temperature at which work hardening is ½ released.] Loss of tensile strength and hardness begins at 550 deg. C. The temperature difference between the beginning of recrystallization and softening is as much as 100 deg. C. and it is doubtful whether the corresponding ranges could be shown to coincide, even if higher magnification had been used.

Jeffries and Archer[10] give 600 deg. C. as the lowest temperature at which new grains visible under a high-powered microscope appear in nickel after severe cold deformation. These authors, however, give no information on the purity of the tested material and time of annealing.

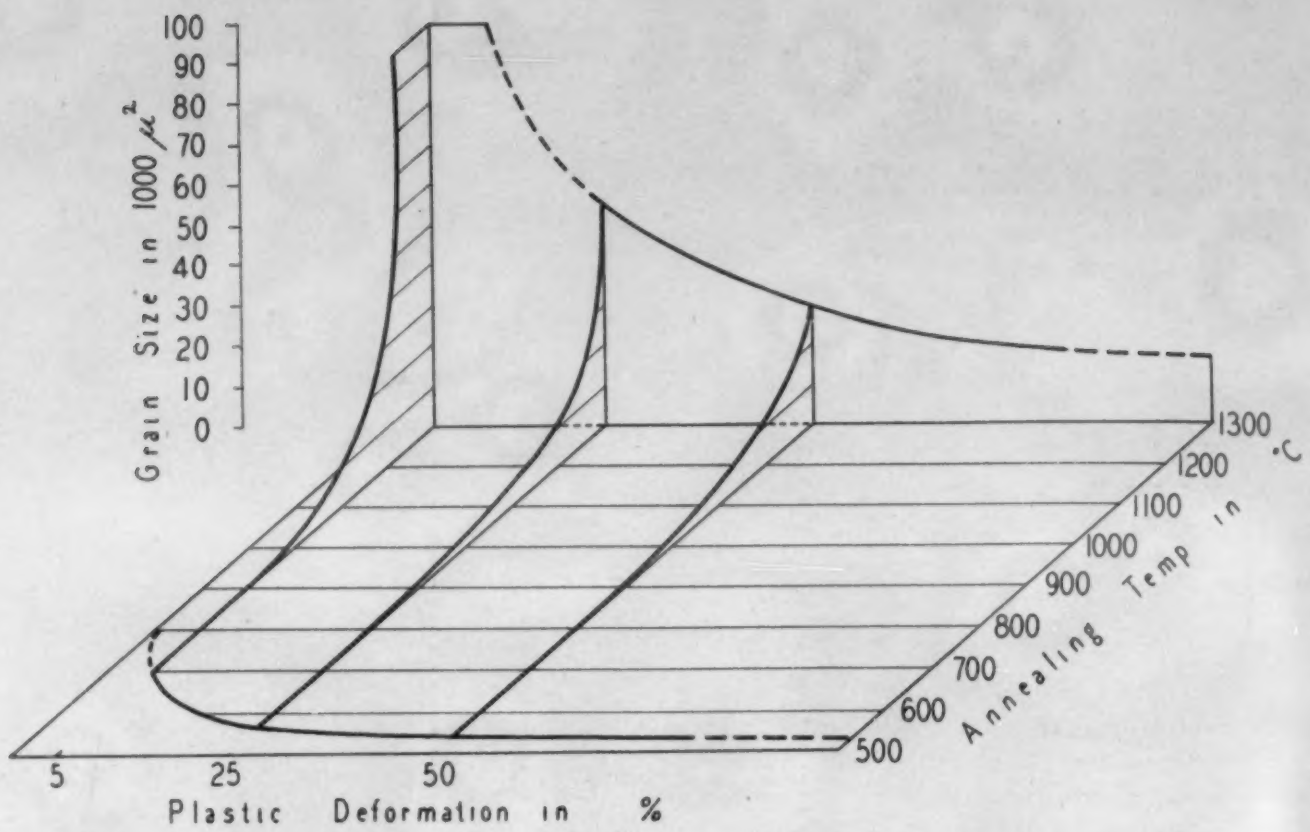

Fig. 1. Recrystallization Diagram of Nickel, after Schottky & Jungbluth (97.92 per cent purity, plastic deformation by upsetting, 1-hr. anneals).

A thorough study of the recrystallization of nickel samples upset 5, 10, 25 and 50 per cent has been carried out by Schottky and Jungbluth.[11] They reported that recrystallization in the sample upset 50 per cent started at 550 deg. C., while marked softening began at about 450 deg. C. Half of the strain-hardening effect was released at $T_r = 510$ deg. C. Their 3-dimensional recrystallization diagram (Fig. 1) shows that the formation of very coarse grain starts, for practical purposes, at temperatures exceeding 1000 deg. C. Increasing the amount of plastic deformation lowers the recrystallization temperature, but grain growth is less pronounced. The latter was most conspicuous at a reduction of 5 per cent (critical deformation). The lowest temperature at which recrystallization started seemed to be about 530 deg. C. with material subjected to the maximum amount of plastic deformation (extrapolation of Fig. 1). In spite of the impurity of their tested material (1.56 per cent Co, 0.47 Mn, 0.04 C, 0.01 S), the softening and recrystallization temperatures reported were relatively low; that they were not higher is probably due to the long annealing time (1 hr.), and the drastic method of cold working (upsetting) employed. With respect to the impurities, the Co content is certainly less effective[1] in raising the recovery temperature than is the Mn contamination. Ransley and Smithells[5] have shown that 0.34 per cent Mn raised the recovery temperature of tensile strength of refined nickel (99.62 per cent) 140 deg. C. (from 410 to 550 deg. C.) the nickel having been previously reduced 75 per cent.

Sizoo[12] failed to find "any trace of recrystallization" in commercially pure (1927 vintage) Mn-bearing nickel submitted to "various degrees of deformation" and annealed over a "wide temperature range." Similarly remelted Mond nickel containing 0.5 to 1 per cent Mn did *not* recrystallize on annealing for 12 hrs. at 1100 deg. C., but if the Mn content was reduced to less than 0.1 per cent, recrystallization could be observed even at 11 magnifications in a sample cold-worked only 2 to 3 per cent. The lowest recrystallization temperature was not determined as the author's object was to correlate grain size with the magnetic properties of pure nickel. Nevertheless, his observation of the drastic effect of manganese on the microscopic recrystallization of nickel is of great significance with respect to the present study.

The "recrystallization temperatures" of different kinds of nickel given by Ransley and Smithells[5] cannot be considered here as they apparently were not based on actual microscopic evidence, but were derived from the author's hardness/temperature curves by taking the end of softening as the "recrystallization temperature." It is the justification for just such assumptions as this that is under present scrutiny.

Ancelle[13] presents an insufficient number of photomicrographs to determine accurately the beginning of recrystallization in nickel wire (99.03 per cent Ni) drawn 23 and 53 per cent. In the sample reduced 53 per cent, some new grains are visible at 650 deg. C; half of the work hardness is released at 640 deg. C. and the beginning of softening occurs at about 600 deg. C.

Dreyer and Tammann[8] state that nickel first completely recrystallizes and then softens, and that the new grains appear at 600 deg. C. Tammann and Moritz[14] found that the hardness of nickel cold worked 60 and 90 per cent recovers at $T_r = 670$ deg. and 660 deg. C., respectively (99.1 per cent Ni, 30 min. anneal).

Scope of the Present Work

In summation it can be said that literature statements on the recrystallization temperature of nickel are very confusing and that vital information—sometimes including the photomicrographs themselves—is usually missing. The lowest graphically evaluated recrystallization temperature reported in the literature is 530 deg. C. and the lowest found by actual microscopic observation is 550 deg. C. Inasmuch as (a) there is no scientific definition of the recrystallization temperature, (b) nickel itself recrystallizes in an extended temperature range rather than at a definite temperature, (c) it is difficult microscopically to find the first indications of recrystallization in any case, and (d) there are structural variations from point to point in the supposedly homogeneous metal, it seems desirable, even

imperative, to submit a complete series of microstructures taken at different temperatures and at close temperature intervals on different kinds of nickel. This will give other investigators an opportunity to interpret critically the submitted experimental evidence, particularly where there may be some quantitative disagreement in conclusions.

Melted carbonyl nickel, pressed carbonyl nickel submitted to *insufficient* working and annealing treatments, and electrolytic nickel, cold-rolled from the as-deposited state, were employed for this cold working and recrystallization study. All samples were etched in a solution of 50 per cent glacial acetic acid and 50 per cent nitric acid. The magnification was uniformly 500 X, the annealing time 30 min., and the heating-up time 1-2 min.

Recrystallization of Melted Carbonyl Nickel

About 100 g. of carbonyl nickel powder of finer than 325 mesh was hydraulically compressed into a slug at 100,000 lbs. per sq. in., slowly heated in hydrogen for 5 min. in a high frequency induction furnace and fully sintered for 10 min. close to the melting point of nickel. A few edge cracks indicated that this temperature must have been exceeded temporarily at the periphery. After it was cooled in hydrogen, the brilliantly silver-white disc was cut with shears in four pieces. The cut surfaces indicated that the sintered slug lacked ductility in the center to a notable degree. The four pieces were then quickly melted in hydrogen in the same furnace using an alundum crucible. The immediately solidified metal was sound and surprisingly soft and ductile, judging from a cut with the shears. The rough surfaces that had been in contact with the crucible walls were ground off and a specimen of uniform thickness was prepared by grinding. A section was reduced 94.6 per cent without any difficulty (from 0.295 in. to 0.016 in. diam.).

Samples annealed for 30 min. at different temperatures yielded the softening curve shown in Fig. 2, curve a. Half of the strain hardening was released at 383 deg. C.; at 426 deg. C. the material had completely softened. The microstructures of samples heat-treated for half an hour at 320, 350, 375, 400 and 426 deg. C. are shown in Fig. 3, a to e, respectively. At 320 deg. C. at few isolated new grains are noticeable and a few streaks of new grains show up at 350 deg. C. These streaks were photographed purposefully, although they appear in isolated spots only and may be due to non-uniform stress distribution in the sample. At 375 deg. C. recrystallization was almost complete. The considerable grain growth at 426 deg. C. is noteworthy.

Recrystallization of melted carbonyl nickel cold-rolled 94.6 per cent apparently takes place, therefore, between approximately 350 deg. and 400 deg. C. It thus appears that the softening range is slightly wider than the temperature range of recrystallization. Owing to the extreme purity of the melted metal of normal density, grain growth is probably less impeded by the grain boundary substance than in ordinary metal of commercial purity.

This recrystallization temperature range is about 200 deg. C. lower than the lowest previous observations, actually made under the microscope, by Schottky and Jungbluth.[11]

Compressed Powder

A study of the recrystallization of nickel made from compressed powder is inviting inasmuch as the softening range has been shown to be shifted to temperatures that are lower the less the number and amount of plastic deformations (and annealings) applied.[2] Furthermore, an unusually large temperature gap between the beginning of softening (700 deg. C.) and the beginning of recrystallization (1500 deg. C.) was observed by Koref[15] on tungsten wire made from powder.

The softening curve of carbonyl nickel that was compressed as powder, sintered in hydrogen, rolled 21.7 per cent, annealed in hydrogen for only 6 hrs. at 1000 deg. C. and then cold rolled 90 per cent from a thickness of 0.173 in. yielded a recovery point of 283 deg. C. with a 30 min. anneal (Fig. 2, curve b). The same samples previously

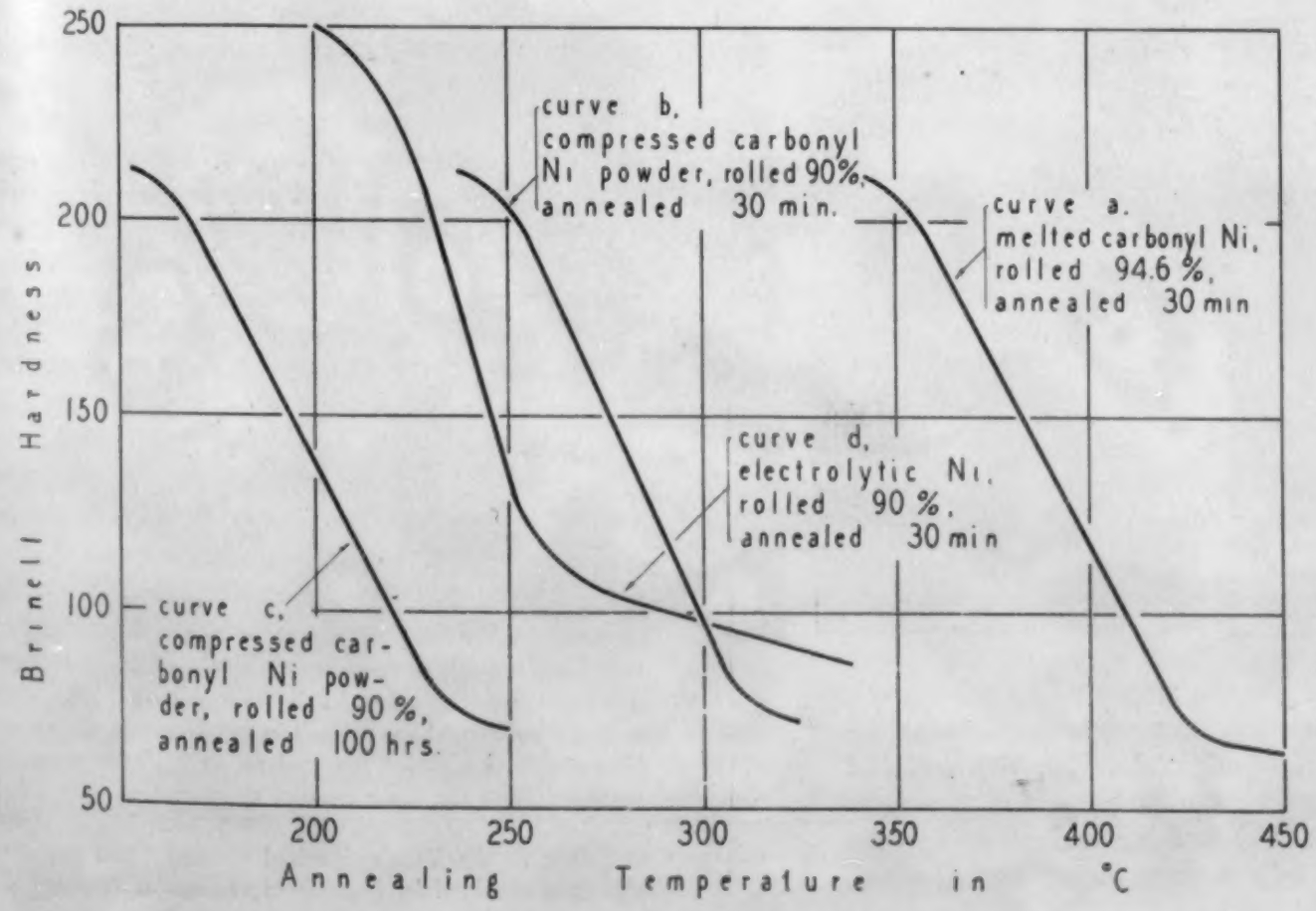

Fig. 2. Softening of Severely Rolled Melted Carbonyl Nickel, Compressed Carbonyl Powder and Commercial Electrolytic Nickel.

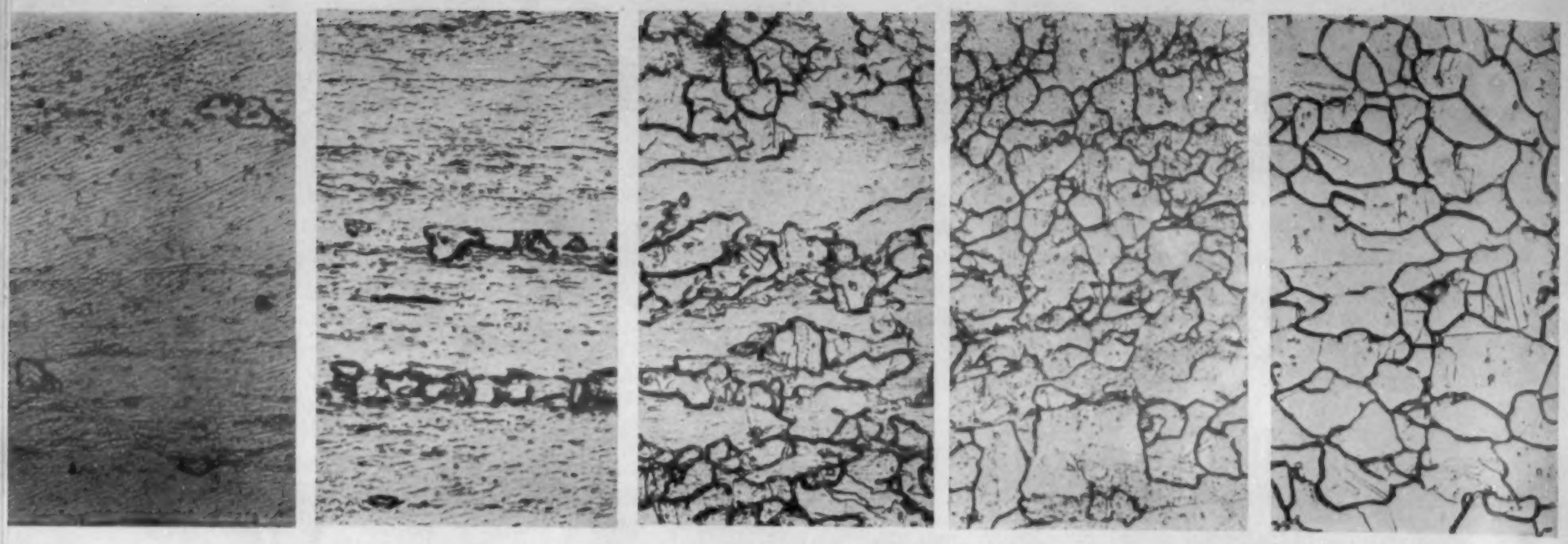

Fig. 3. Effect of Rising Temperatures on the Microstructure of Melted Carbonyl Nickel Cold Rolled 94.6 per cent (30-min. Anneal). Left to right: 320, 350, 375, 400 and 426 deg. C. (a to e.)

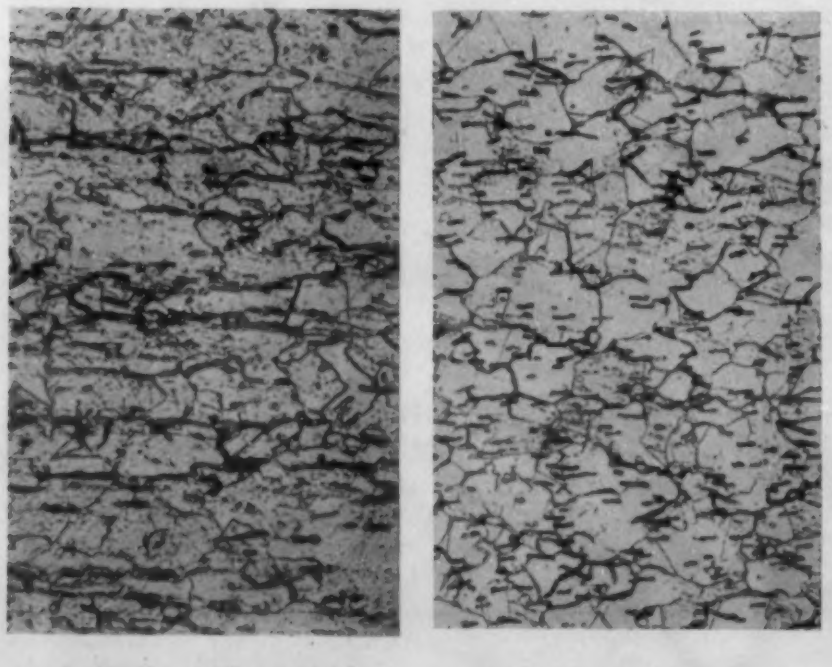

Fig. 4. Effect of Rising Temperatures on the Microstructure of Compressed Carbonyl Nickel Powder Cold Rolled 90 per cent (30-min. Anneal). Left to right, top row: as-rolled, 250, 275, 300; bottom row: 325, 400 and 502 deg. C. (a to g.)

used for hardness testing[2] were submitted to microscopic examination. The microstructures observed in the as-rolled condition and at 250, 275, 300, 325, 400, and 502 deg. C. are presented in Fig. 4 a to g.

Owing to insufficient cold working and annealing, the density of this material falls short of that of melted metal.

Note: The purity of this material is undoubtedly higher than that of the melted carbonyl nickel. The powder sample always rested on pure carbonyl nickel. An analysis of a similarly-treated specimen[3] prepared from the same powder yielded: Less than 0.001 per cent Co, 0.005 Cu, 0.001 Si, and 0.045 Fe. The C determination according to the Yensen method showed 0.002 per cent C as occluded gas, obtained by heating in vacuum at 600 deg. C.

for 10 min., and 0.0045 per cent C by burning in oxygen at 1150 deg. C.

Voids may be seen in the as-rolled sample. The first new grain boundaries faintly appear at isolated spots at 250 deg. C., at which temperature softening also starts. The recovery of hardness is completed around 320 deg. C. and the same may be said about the recrystallization. In contradistinction to the melted carbonyl nickel, grain growth is much more impeded in the compressed powder sample. Although the former begins to recrystallize at temperatures 100 deg. C. higher than the latter, higher temperatures are required to produce the same coarse grain in the powder samples, as compared to the melted material. The powder sample exhibits coarse grain on annealing at 502 deg. C.

It had previously been found[8] that the hardness recovery of powder samples does not follow the same laws on prolonged heating as metal that has solidified from the liquid state. The plastically deformed powder samples softened at a much faster rate. Fig. 2, curve c, shows the effect of a 100-hr. anneal on the 90 per cent cold-rolled material. Half of the work hardening is abolished at 197 deg. C. The microstructure (Fig. 5) of a sample annealed for 100 hrs. at 193 deg. C. at which temperature the hardness had dropped from 212 Brinell to 160 Brinell, clearly shows partial recrystallization. Hardness recovery and recrystallization seem to occur simultaneously also on long-time annealing.

Thus it can be said that the temperature range of recrystallization and that of hardness recovery of compressed powder samples are the same, in spite of their porosity. The recrystallization temperatures reported—between 200 and 300 deg. C.—are the lowest yet observed on nickel.

Electrolytic Nickel

To the best of the author's knowledge, nothing has been published on the recrystallization of electrolytic nickel, *cold-worked without previous annealing*. The grain growth in nickel in the electro-deposited state on annealing at different temperatures has been systematically studied by Jenicek.[16] He found no structural changes to occur during a 20-hr. anneal at 480 deg. C.; slight changes were observed in the temperature range of 550 to 650 deg. C., and grain coarsening developed after heating to temperatures exceeding 1000 deg. C. The softening curve of this material shows that the hardness of the electro-deposited metal is ½ reduced at 496 deg. C. Apparently the temperature ranges of softening and recrystallization do not coincide. According to McNaughton and Hothersall[17], after a 4-hr. anneal at 1000 deg. C. the hardest deposit of nickel (which incidentally had the finest grain structure) showed no sign of grain growth.

In the present experiments, a 6 x 6 in. plate of a commercial brand of electrolytic nickel was prepared as described later. A typical recent analysis[18] of this material shows it to contain 99.95 per cent Ni + Co, 0.01 Cu, 0.01 Fe, and 0.001 S. The uneven surface of the plate was removed by milling it to a uniform thickness of 0.265 in. This as-deposited metal was then cold-rolled 90 per cent without any edge-cracking. Samples annealed for 30 min. at different temperatures gave the softening curve d, Fig. 2. Miscrostructures of the same samples are presented in Fig. 6 a-f, the following temperatures being studied: 200, 228, 251, 325, 400 and 498 deg. C. In contradistinction to Jenicek's observations on nickel in the electrodeposited state, without cold rolling, the formation of new grains and the loss of total hardness (work hardness superimposed on the hardness due to electrodeposition) begin at the same temperature in cold-rolled electrolytic nickel. Fig. 6 b shows that new grain boundaries begin to develop at 228° deg. C., at which temperature the hardness has dropped from 260 Brinell to 215 Brinell. Significant grain-coarsening, however, does not occur below 500 deg. C. Lateral grain growth is relatively slight in hard nickel deposits, owing to segregation of non-metallic material at the grain boundaries, according to MacNaughton and Hothersall.[17] Whether the same conditions hold for severely cold-worked electro-deposited nickel annealed at only 228-500 deg. C. is hard to say. We confine ourselves to concluding that the kinetics of grain growth in the three different kinds of nickel evidently varies to a remarkable extent, whereas their temperature range of recrystallization and hardness recovery are practically the same, under the testing conditions applied in this investigation.

Fig. 5. Microstructure of Compressed Carbonyl Nickel Powder Cold Rolled 90 per cent and Annealed for 100 hrs. at 193 deg. C.

Discussion

The low recrystallization temperatures observed on the melted carbonyl nickel remove a previously inexplicable exception to the rule that the lowest temperature (T_ρ) at which atoms begin to change places is ⅓ of the absolute melting point (T_s). In an evaluation by Botschwar,[19] recrystallization temperatures of 660 and 530 deg. C. have been used for nickel to derive $T_\rho/T_s = 0.46 — 0.54$. This coefficient becomes 0.36 when taking into account the beginning of recrystallization observed at 350 deg. C. in melted carbonyl nickel. This brings nickel in line with other metals that have been studied in the highly pure state.

For the compressed carbonyl nickel powder this factor would become 0.30 using an observed recrystallization temperature of 250 deg. C., and 0.29 for cold worked electrolytic nickel, which was found to start recrystallizing at 225 deg. C. The negative deviation from the theoretical factor by the latter two materials is undoubtedly due to the fact that both materials differ from melted solid material, the compressed powder as to porosity and the electrolytic nickel as to grain size. The atoms are affected by the cold work to a much greater extent than in solidified metal. Thus the vibration amplitude of the atoms and their mobility in the lattice is increased. The effect of cold work on the increased diffusion speed has been previously discussed at length [20, 21] and experimentally proved by comparing precipitation hardening in annealed and in cold-worked metallic materials.

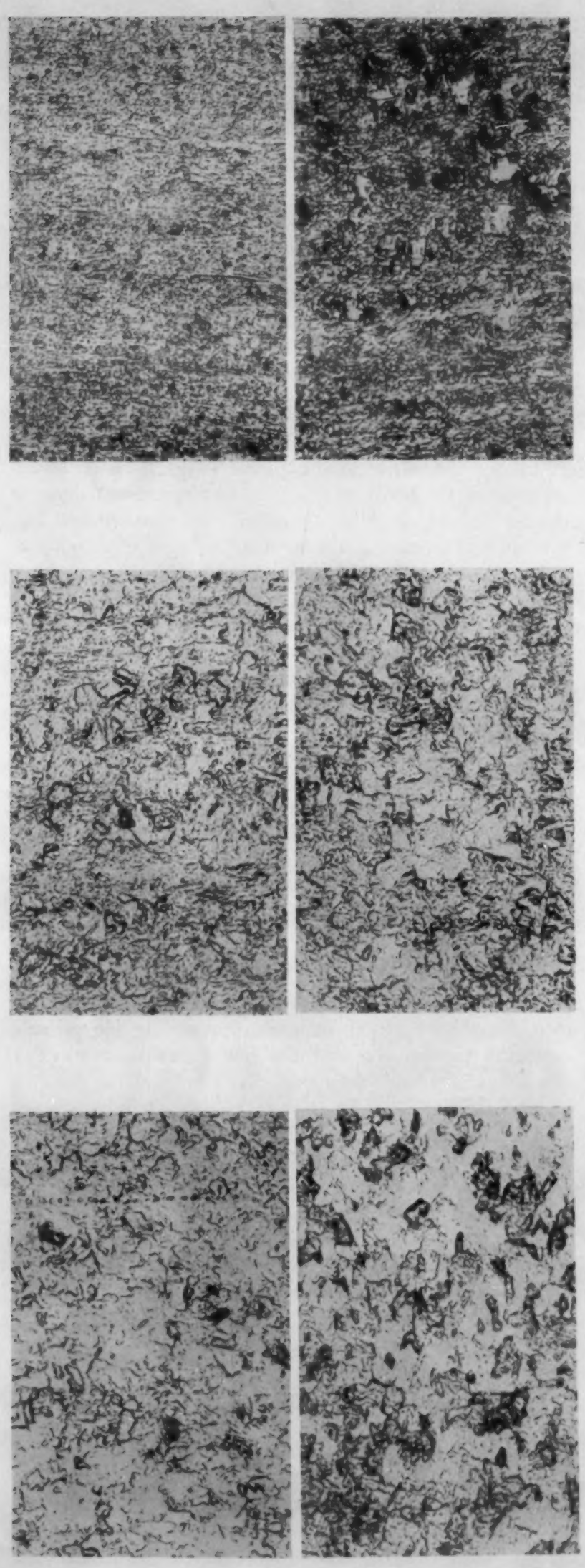

Fig. 6.—Effect of Rising Temperatures on the Microstructure of Electrolytic Nickel Cold Rolled 90 per cent (30-min. anneal). Left to right, top: 200, 228, middle: 251, 325; bottom: 400 and 498 deg. C. (a to f.)

Summary

The temperature ranges of microscopically observed recrystallization and of release of hardness after cold rolling were found practically to coincide in severely wrought melted carbonyl nickel, compressed carbonyl nickel powder and electrodeposited nickel. However, the kinetics of grain growth is markedly different for these materials.

In melted carbonyl nickel, the beginning of recrystallization was found at 350 deg. C., which temperature is 200 deg. C. lower than the lowest recrystallization temperature of nickel microscopically found by previous investigators. This discrepancy is attributed primarily to the relative impurity of the nickel used in former tests.

Beginning of microscopic recrystallization was found at 250 deg. C. in compressed, insufficiently worked carbonyl nickel powder (90 per cent reduction), at 350 deg. C. in melted carbonyl nickel (94.6 per cent reduction) and at 228 deg. C. in commercial electrolytic nickel (90 per cent reduction), employing, in each case, a 30-min. anneal.

Compressed carbonyl nickel powder cold rolled 90 per cent was found to have partly recrystallized below 200 deg. C. during a 100-hr. anneal.

Acknowledgment

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THE RELATION BETWEEN THE

Grain Areas on a Plane Section

AND THE GRAIN SIZE OF A METAL

by J. J. B. Rutherford, R. H. Aborn, and E. C. Bain

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THE METHODS OF ESTIMATING GRAIN-SIZE in a metal, with the possible exception of the method based on a rating of the texture of the fracture of a hardened steel specimen, depend upon a comparison of the grain-boundary network revealed on microscopic examination of a plane surface of a specimen, with a series of graded standard networks, either typical micrographs or idealized patterns. The plane examined is in effect a random section through an assemblage of solid grains, and consequently the network observed comprises sections of grains ranging in size up to the maximum possible cross sectional area of any grain in that plane. In other words, on the random plane section there is a *range* of grain areas even when all of the grains are in fact of equal volume; thus the true grain size is, in general, more uniform than the apparent grain size indicated by the range of grain areas observed on a representative plane surface through the specimen.

This reasoning, which has been verified in specimens of stainless steel and of brass purposely disintegrated by intergranular corrosion, indicates that minor differences in apparent size as observed on a plane section have little real significance with respect to the properties of the metal. Thus it is of interest to consider the relation between this grain area and the real size (or mean volume) of the metal grains, for it is the latter which, either directly or indirectly, correlates with the useful properties of the metal. In doing this we shall first discuss an idealized case in which all of the grains are assumed to be spherical and identical in size.

Distribution of Grain Sizes on a Plane Section of a Solid Composed of Spherical Identical Grains.

In order to ascertain the relation between the significant real grain size and the "grain size" observed on a plane section, let us assume that the grains are all spherical, the simplest geometrical form, and equal in size. This assumption cannot be strictly valid, for an assemblage of spheres cannot be arranged completely to fill space; but it is amply accurate for our present purpose of ascertaining the general statistical distribution of grain areas, in view of the fact that in most metals, as examined for grain size, the grains are not far from spherical. To this question we shall revert later.

The area (A) of a plane section of a sphere of unit radius ranges from π to 0, depending upon the distance (x) of the plane from the center of the sphere, in accordance with the formula $A = \pi(1 - x^2)$. The relative areas for ten equidistant values of x are given in Table I.

Table I. Relative Areas of Plane Sections of a Unit Sphere.

Distance of plane from center, x	Percentage of radius of sphere, $X=100x$	Relative area of section, $(1-x^2)$	Percentage of maximum area, $100(1-x^2)$
0	0	1.00	100
0.1	10	0.99	99
0.2	20	0.96	96
0.3	30	0.91	91
0.4	40	0.84	84
0.5	50	0.75	75
0.6	60	0.64	64
0.7	70	0.51	51
0.8	80	0.36	36
0.9	90	0.19	19
1.0	100	0.	0

If a plane cuts through a random assemblage of equal unit spheres, the chance that it cuts any sphere at a given value of x is the same as the chance when an unlimited number of planes cut a single sphere; moreover these planes may be taken as parallel because of the symmetry of the sphere. Now if we think of the radius perpendicular to these parallel planes, it is clear that the chance of cutting this radius at a distance between x' and x'' is equal to $x' - x''$ or in percentage to $(X' - X'')/100$ where $X = 100x$. Thus the last column of Table I represents, for ten equally spaced values of x, the relative distribution of the circular areas which would be observed on a plane section of a random group of unit spheres. For instance,

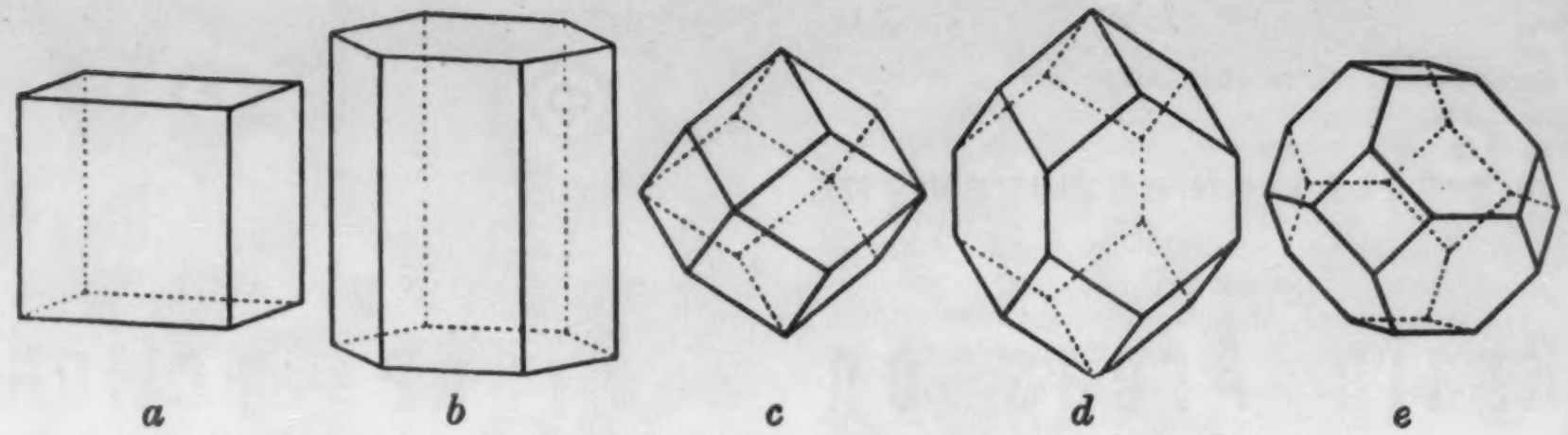

Fig. 1—The Five Regular Solids, Any of Which with Mere Duplications Can Completely Fill Space: (a) Cube (b) Hexagonal prism (c) Rhombic dodecahedron (d) Elongated dodecahedron (e) Cubo-octahedron (Kelvin's 14-plane-faced solid). (From Tutton's "Crystallography and Practical Crystal Measurement," Fig. 585).

10 per cent of all the "grains" would appear to range in area from 0 to 19 per cent of the unit area, another 10 per cent from 64 to 75 per cent of the unit area, and so on.

The values in this table are not quite those in which our interest centers, which is the frequency of appearance of a "grain" of size within specified limits. This can be derived either from the data of Table I by an appropriate plot of x against $(1 - x^2)$, or by substituting, in the formula above, the specified values of the area and calculating the corresponding values of x (or X). When this is done for ten equally-spaced values of A, we get Table II, which shows the frequency of appearance of "grains" within each of the several ranges of size. For instance, if a plane cuts a random assemblage of unit spheres, the area of the maximum section (that is, the great circle) being rated as 100, about 31 per cent of the circular "grains" will have an area between 90 and 100, 14 per cent between 80 and 90, and so on.

Table II. Frequency of Appearance of "Grains" Within Specified Limits of Size When a Plane Cuts a Random Group of Unit Spheres.

Range of "grain-size" in terms of maximum as 100	A.S.T.M. grain size	Approximate relative frequency of appearance
100-90		31
90-80		14
80-70		10
70-60		8
60-50		8
50-40		7
40-30		6
30-20		6
20-10		5
10-0		5
		100
100-50	N	71
50-25	$N+1$	16
25-12.5	$N+2$	7
12.5-0	all finer	6
		100

The usual A.S.T.M. "grain size" number covers a range from a specified maximum area to one-half of that area. Thus the rating N (for instance, No. 2) would in our notation cover the range from 100 to 50, and the frequency of its appearance (in the ideal case of spherical particles all equal in size) would, from Table II, be 31 + 14 + 10 + 8 + 8 or 71 per cent. Similarly the rating $N + 1$ (e.g. No. 3) covers the range 50 to 25, and its frequency would be 7 + 6 + 3 or 16 per cent; the rating $N + 2$ (e.g. No. 4), with a range of 25 to 12.5, would have a frequency of about 7 per cent; and all finer ratings together an aggregate frequency of about 6 per cent. Thus in this ideal case, although all of the grains actually correspond to No. 2 size, only 71 per cent would appear to do so, while 16 per cent would appear to be No. 3 and 13 per cent to be still smaller. These figures, summarized at the bottom of Table II, apply strictly only to the idealized case of really spherical identical grains, but this general distribution is believed to hold substantially for the frequency of "grain sizes" observed on a plane section of a metal composed of grains of nearly the same actual size.

Another example may be given by answering the question of what would be the ideal distribution of grain size ratings on material half of whose grains are of size corresponding to N, the other half of size $N + 1$. The answer is readily derived from the data of Table II, as follows in Table III.

Table III. Relative Frequency of Appearance of "Grain Sizes" on a Plane Through an Ideal Specimen Composed of Equal Numbers of Grains of Sizes N and N + 1.

	On 50 grains size N	On 50 grains size $N+1$	Total frequency per cent
Rating N (e.g., No. 2) ...	35.5	...	35.5
$N+1$ (e.g., No. 3)	8	35.5	43.5
$N+2$ (e.g., No. 4)	3.5	8	11.5
All finer	3.	6.5	9.5
	50	50	100

Thus in this case of equal real frequency, there would appear to be appreciably more (43.5%) of size $(N + 1)$ than of size N (35.5%). These examples emphasize that good judgment must be used if grain size estimations made on a plane section are to be interpreted correctly in terms of the distribution of actual grain sizes within the metal.

To return now to the case of a group of identical spheres, the frequency of the several ratings would be as stated above if the observer counted them; but if, as is not improbable, he estimated the proportion of the field occupied by the several sizes, his rating would be in accord with the last column of Table IV, indicating that he would then tend to underestimate the relative number of the smaller areas visible in the section.

Table IV. Relative Area Occupied by the Several "Grain Sizes" on a Plane Section Through Spheres of Identical Size.

Rating	Range of area	Mean relative area per grain A'	Relative number of grains (from Table II) n	Aggregate relative area for each size nA'	Percentage of total area occupied by each apparent grain size $100nA'/\Sigma nA'$
N	100-50	75	71	5325	87
$N+1$	50-25	37.5	16	600	10
$N+2$	25-12.5	18.75	7	131	2
All finer	12.5-0	6.25	6	37	1
				6093	100

These statistical analyses of idealized cases are in general harmony with experience. They indicate strongly that whenever one sees that about nine tenths of the area examined comprises grains within a single A.S.T.M. grain size number, one may be assured that the specimen is extremely uniform in actual grain size. They indicate moreover that small proportions of sizes, smaller than the most common size present, should not be reported unless in clusters[1], and raise the question as to whether too much attention is not being paid to minor differences in the "grain size" microscopically observed. Indeed for practical purposes, it would seem that four or five unit ratings should be ample, in place of the eight (or more) now commonly used; and that subdivisions between the present unit ratings are absurd. In an actual steel *minor* differences in real grain size have little effect on the hardenability of the steel and on the residual stress pattern in the hardened steel, hence on the toughness and usefulness of the finished steel.

The Actual Shape of the Metal Grains in a Crystal Aggregate.

The foregoing statistical deductions are based on the assumption that all the grains are spherical, an assumption which cannot be strictly true yet introduces no serious error in the results presented. There are only five regular solids which can by mere duplication fill space; these are illustrated in Fig. 1, the solid becoming more nearly spherical as the number of faces increases.

Even in the case of the cube, which is the farthest from the sphere, the distribution of areas in a plane section would be qualitatively similar to that computed above for the sphere. A random plane section through an assemblage of cubes would show 3-, 4-, 5- or 6-sided figures, as illustrated in Fig. 2; and the areas observed would depend upon the angle between the plane and the cube-faces and upon the distance between the plane and the center of each cube. The area of a section through a cube of unit dimensions ranges, according to the number of sides which bound it, between the values shown in Table V. The fourth and fifth columns give the ratio of the minimum and maximum area respectively to the largest possible area of cross-section, namely that through the diagonal of the cube, of area $\sqrt{2}$; for example, the area of the smallest 5-sided section is $\sqrt{8/16}$, which is just one-half of this maximum. This geometrical illustration shows that, in a random plane section of cubic grains, the aggregate area of 3-sided figures would be noticeably smaller than that of the 4-, 5- or 6-sided figures, and that 5- and 6-sided figures would constitute the greater part of the whole area of the section.

Table V. Figures Visible on a Plane Section of an Assemblage of Cubes.

Number of sides of plane figure	Area of section		Ratio of this area to maximum possible	
	Minimum	Maximum	Minimum	Maximum
3	0	$\sqrt{12/16}$	0	0.62
4	0	$\sqrt{32/16}$	0	1
5	$\sqrt{8/16}$	$\sqrt{32/16}$	0.50	1
6	$\sqrt{27/16}$	$\sqrt{32/16}$	0.92	1

In an aggregate of crystals, regardless of the geometrical form assumed during free growth, the inevitable interference results in the formation of polyhedra or of more complex interlocking forms. Desch[2] compared the frequency of occurrence of interface polygons in foam-cells with that of external surface polygons in a disintegrated

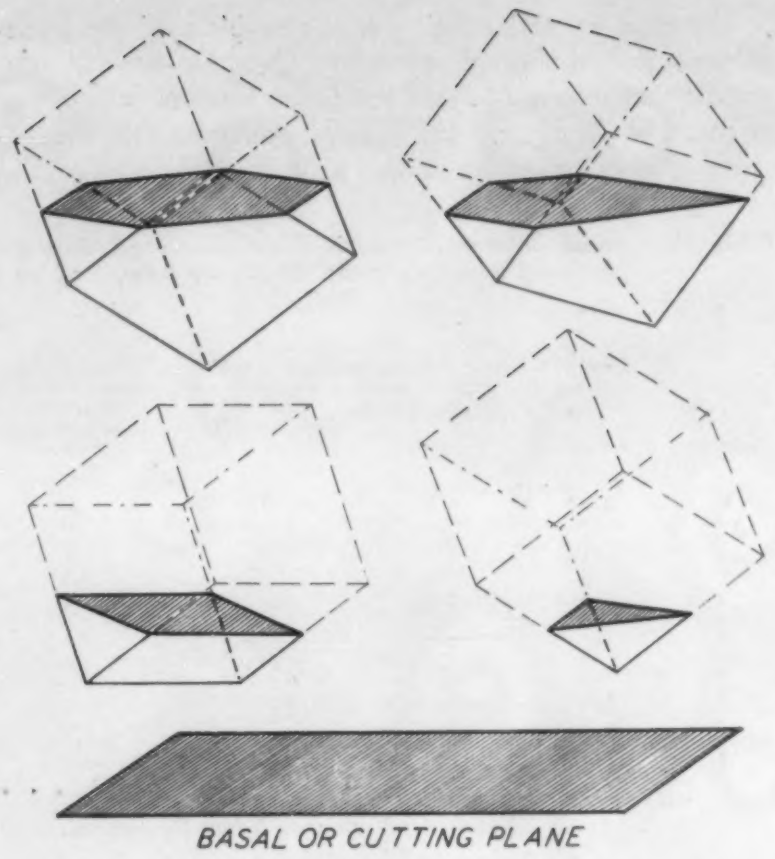

Fig. 2.—Types of Plane Sections of Identical Cubes.

brass and an embrittled chromium steel, and found that the frequency curve was almost identical in all three cases, five-sided faces being by far the most frequent. "In fact, the individual cells tend to approximate to the pentagonal dodecahedron, slightly distorted by curvature so that all the faces may meet at an angle of 120 deg., as required for equilibrium between films. Space cannot be completely filled by such dodecahedra, and the cells are found to vary about that figure as a mean, gaps being filled by small tetrahedra and hexahedra. The distribution of the original nuclei is not likely to be perfectly regular, but observation of normal cast metals suggests that the size of the grains does not vary widely, so that the nuclei must have been spaced uniformly on the average. It is not possible to determine the shape of the polyhedral grains from an examination of their cross sections, but the general picture is quite consistent with the above results."[3]

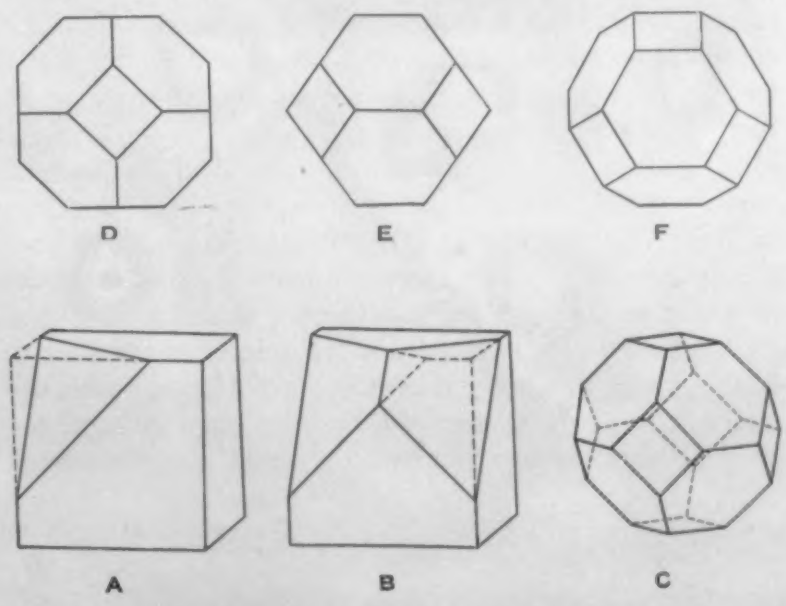

Fig. 3.—The Formation from a Cube and the Appearance of the Kelvin 14-Faced Solid Figure (Tetrakaidekahedron).

The most general solution of the problem of the homogeneous partitioning of space was given by Kelvin[4] who proved that it is a 14-faced solid, the faces of which may or may not be plane. He showed moreover that the 14-faced solid of minimum surface area has eight 6-sided and six 4-sided faces, all the edges being equal in length, but curved into plane arcs. The plane-faced counterpart of this interesting figure can be constructed by cutting away the eight corners of a cube on (111) planes until only half of the cube volume remains; the intersection of the cube edge with the (111) cutting planes will always be at a distance of three-quarters of the cube edge from the removed corner as shown in Fig. 3 *a, b,* and *c*. This solid figure, three views of which are shown in Fig. 3 *d, e, f,* is the most nearly spherical of all the regular solids which may with mere duplication completely fill space.

This is the form which will *tend* to be assumed by each of an assemblage of growing crystals, because the most thermodynamically stable (that is, the most probable) state is that in which the area of the interface is a minimum. As a matter of fact, well annealed metal comprises grains with from perhaps 9 to 19 faces, and on the average about 14 faces. This shows that the equilibrium, or stable, state is being approached in fact, though we cannot expect that it will be fully realized. Therefore we feel justified in assuming, as the limiting case, the formation of the 14-faced solid, and on this basis calculating the ideal relations between number, size and surface area of grains, as set forth in Table VI. We consider the values of Table VI to be of the right order of magnitude; for even if the calculations are made on the extreme basis that the grains are all cubic (the regular space filling solid of minimum number of faces), the results differ from those given by less than corresponds to a whole grain-size rating. As a practical test of these data, some estimations of grain size were made upon samples of 18-8 stainless steel, which were subsequently disintegrated completely by severe intergranular sensitization followed by corrosion in a sulphuric acid-copper sulphate solution; a careful count of the separated grains showed the number to correspond well with that derived from the "grain size" estimated from the microscopic examination.

Table VI. Ideal Relation Between Grain Size, and Average Number, Diameter, Cross-Sectional Area of Grains, and Total Interfacial Area; Columns VI-IX are calculated on Basis of the 14-Faced Solid of Minimum Surface Area.

I	II	III	IV	V	VI	VII	VIII	IX
A.S.T.M. grain-size number	Mean number of grains per sq. in. as viewed at 100X	Mean area of cross-section of a grain: As viewed at 100X sq. in.	Mean area of cross-section of a grain: True size sq. mm.	Diameter of cross-section of equivalent spherical grain mm.	Mean number of grains per: cu. in.	Mean number of grains per: cu. mm.	Mean total interfacial area: sq. in. per cubic inch	Mean total interfacial area: sq. mm. per cubic mm.
N	$n=2^{N-1}$	$A'=1/n$	$A=0.0645A'$	d	m'	m	S'	S
−1	0.25	4.	0.258	0.574	92,100	5.6	125.	4.7
0	0.5	2.	0.129	0.406	261,000	15.9	170.	6.7
1	1.	1.	0.0645	0.287	739,000	45.1	240.	9.5
2	2.	0.5	0.0323	0.203	2,090,000	128.	340.	13.4
3	4.	0.25	0.0161	0.144	5,910,000	360.	480.	18.9
4	8.	0.125	0.00806	0.101	16,700,000	1,020.	679.	26.7
5	16.	0.0625	0.00403	0.0718	47,300,000	2,880.	961.	37.8
6	32.	0.0313	0.00202	0.0507	134,000,000	8,160.	1360.	53.4
7	64.	0.0156	0.00101	0.0359	378,000,000	23,000.	1920.	75.6
8	128.	0.0078	0.000504	0.0254	1,070,000,000	65,300.	2720.	107.
9	256.	0.0039	0.000252	0.0179	3,030,000,000	184,000.	3840.	151.
10	512.	0.0020	0.000126	0.0127	8,560,000,000	522,000.	5430.	214.
11	1024.	0.0010	0.000063	0.0090	24,200,000,000	1,470,000.	7690.	302.

Notes to tables:

Column IV. In German usage this area is expressed in terms of μ^2, where $\mu = 0.001$ mm.; to transform to German units, the numbers given in this column have to be multiplied by 1,000,000.

Column V. $d = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4}{\pi} \cdot \frac{0.0645}{n}}$ This column is in terms of the units commonly used for non-ferrous metals.

Column VI. $m' = \frac{1}{8\sqrt{2}l^3}$, where l is length in inches of edge of any of the 14 faces; the volume of the solid is $8\sqrt{2}l^3$. Its maximum cross-section area is $7l^2$, or $\frac{1.7}{10000n}$ when expressed in sq. in.; its surface area is $l^2(6 + 12\sqrt{3})$.

Column VII. $m = \frac{m'}{16390}$

Column VIII. $S' = \frac{l^2(6 + 12\sqrt{3})}{2(8\sqrt{2}l^3)}$

Column IX. $S = S' \frac{645.2}{16390}$

Conclusion.

The statistical distribution of apparent grain sizes, as observed on a plane section may, unless logically considered, give an incorrect impression of the real grain size in the direction of indicating the presence of a larger proportion of the smaller sizes than is in fact present. These considerations corroborate our general experience in leading us to believe that none of the smaller grain sizes should be regarded as being comprised in the metal unless they appear to be present, first of all, in clusters, and otherwise to the extent of, say, 10 per cent of all the grain sections; also that it is seldom useful to report more than a single grain size, except when there are considerable quantities of two separate sizes, this being an indication that the temperature-time schedule has been such that marked coarsening has begun but has not proceeded to completion.

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[1] Compare *Metals Handbook*. Amer. Soc. Metals, Cleveland, 1936, p. 594.
[2] *J. Inst. Metals*, Vol. 11, 1914, p. 57.
[3] C. H. Desch. "Chemistry of Solids," Cornell Univ. Press, 1934, p. 61: *Rec. trav. chim.*, Vol. 42, 1923, p. 822.
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Is Beryllium Ductile?

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SINCE WOEHLER PREPARED BERYLLIUM in the form of powder, more than one hundred years ago, many investigators have claimed the element should be ductile and have tried to prove this—unfortunately without much success. For example, F. Fichter and K. Jablczynsky[1] asserted that beryllium is ductile at high temperatures, but they do not appear to have given sufficient proof of their claim. The author himself[2] eleven years ago found that beryllium of 99.9 per cent purity is quite brittle under all conditions and not rollable at all. On the other hand, Sloman,[3] observing on a small sample of distilled metal slip bands at the Brinell impression, concluded from this that beryllium was to a certain extent malleable, if quite pure. Using Sloman's method, with certain improvements, the writer[4] later distilled larger quantities of the element and found no ductility. Hausser, Bardehle, and Heisen[5] developed a method for making beryllium plates for X-ray windows by hot drop forging. This proved that a certain degree of malleability exists.

General Aspect of the Question

Beryllium, as the first element of its group, must possess properties of the neighboring classes of elements. Its alloys with other metals have a striking resemblance to those of silicon with the same. The equilibrium diagrams of the binary alloys of both these metals with Ag, Al, Cu, Zn, Ni and Fe have very similar characteristics. Beryllium, however, does not alloy with Mg, being dissimilar to Si in this regard.

The malleability may depend to a large extent on the crystal structure. Beryllium crystallizes in the close

Fig. 1. Disposition of the Crucible and Condensing Hood.

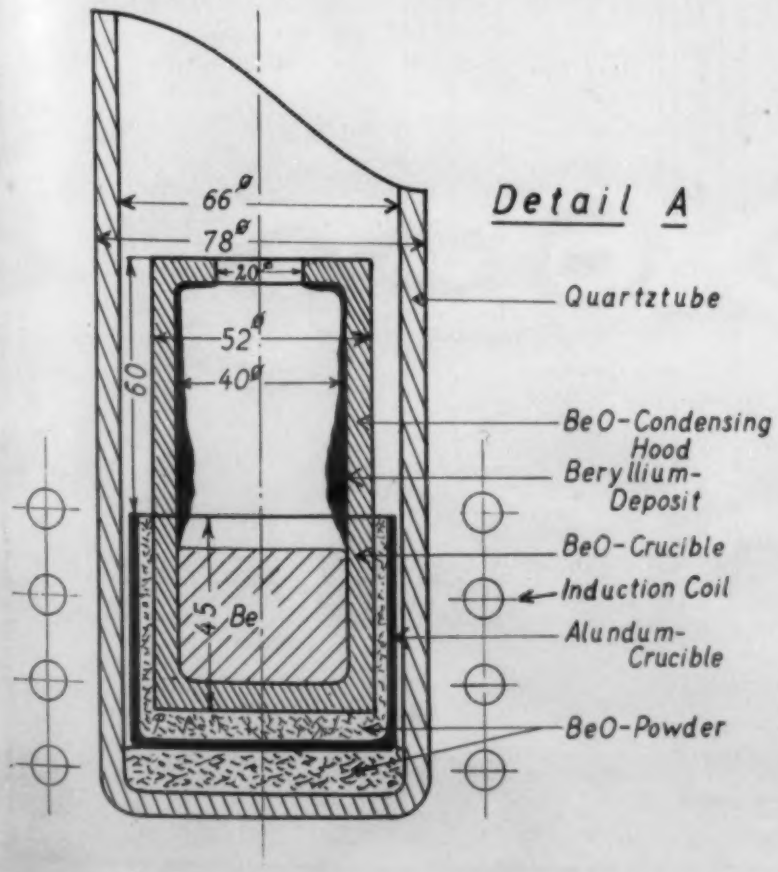
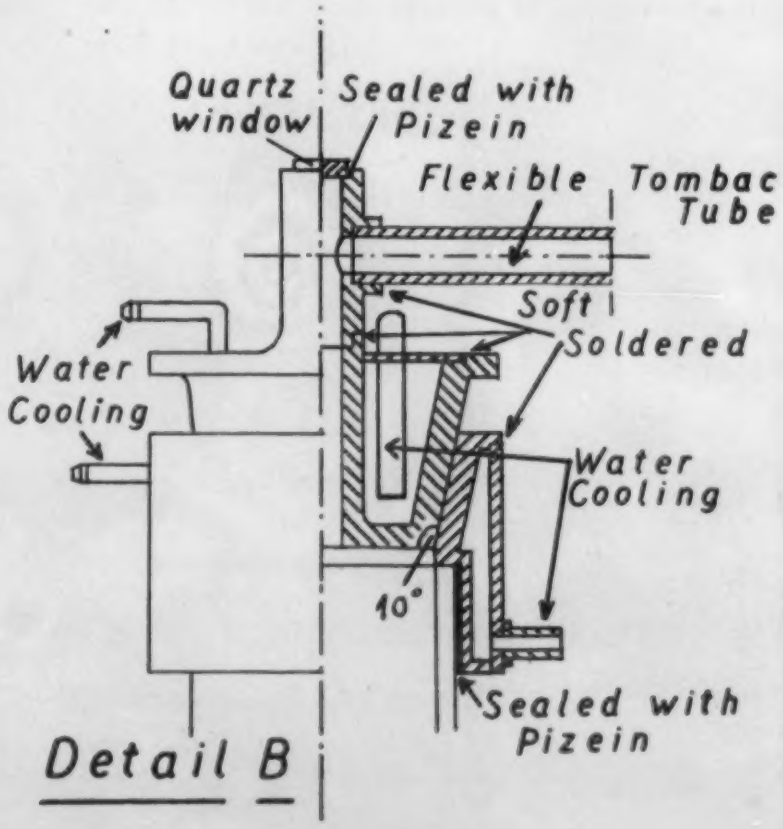


Fig. 2. Furnace Head.



packed hexagonal system, but several authors have suggested that perhaps two allotropic modifications prevail.[6] The hexagonal metals usually have a low ductility. It is, however, possible that beryllium, like Ca, when heated, changes its hexagonal crystal structure into another more malleable one.

It is known that the binary alloys of Be and Al are malleable, even up to 70 per cent. The beryllium crystals are strained and show certain signs of ductility. But with higher beryllium contents, rolling gets more and more difficult, and the alloy breaks up. The malleability of a metal must be considered from a practical point of view. We know some metals which are ductile when hot, but quite brittle when cold, like bismuth. Recent research has enlarged considerably our knowledge about metals of this type. For example, Cr, Ti and W can to some extent be hot rolled, but break when bent cold. Such metals are worthless for structural purposes, but are used for many special applications. In another group, we have the metals with good ductility in both the hot and cold condition, and it is these which are employed for general engineering work. Beryllium does not appear to belong in the latter class, and there seems no hope of ever seeing this metal used in light weight construction.

The Distillation Method of Purification

Brunner[7] found that if beryllium is heated in hydrogen at 5 mm Hg in a BeO-tube at 1530 deg. C., it evaporates to the cold end. Sloman[3] has shown a way to prepare beryllium in a much purer state by distilling it in vacuum. The writer improved this method by working with larger lots in an absolute vacuum below 0.001 mm Hg, using a beryllia condensing hood.[4] The vapor pressure of beryllium as a function of the temperature was given by Bauer and Brunner[8]. It boils, according to these authors, at 3040 deg. abs. at 760 mm Hg, and at 1780 deg. abs. at 1 mm Hg. Its vapor-pressure appears, therefore, to be higher than that of Al and Si (1880 deg. abs. and 1910 deg. abs. resp.) and lower than that of Mn (1540 deg. abs.). These figures, taken from a recent publication of Euken[9] probably should be accepted with caution.

In distillation experiments of this type, the boiling characteristics of alloys must be taken into consideration. One may have a lowering of the vapor pressure from impurities, due to the formation of stable compounds. A typical case is that of manganese, the evaporation of which can be stopped almost completely by the addition of carbon. On the other hand, one may find as in the case of alcohol-water that some impurities like bismuth in lead, or nickel in iron, cannot be expelled completely by distillation as, starting from a certain low content of Bi in lead or Ni in iron, mixtures of constant composition evaporate.

Difficulties of this type are met with in the distillation of impure beryllium. For example, a small amount of metal produced by Siemens & Halske, of about 99 per cent purity, was distilled in a good vacuum, using the apparatus described below. The distillate and residue showed the following composition:

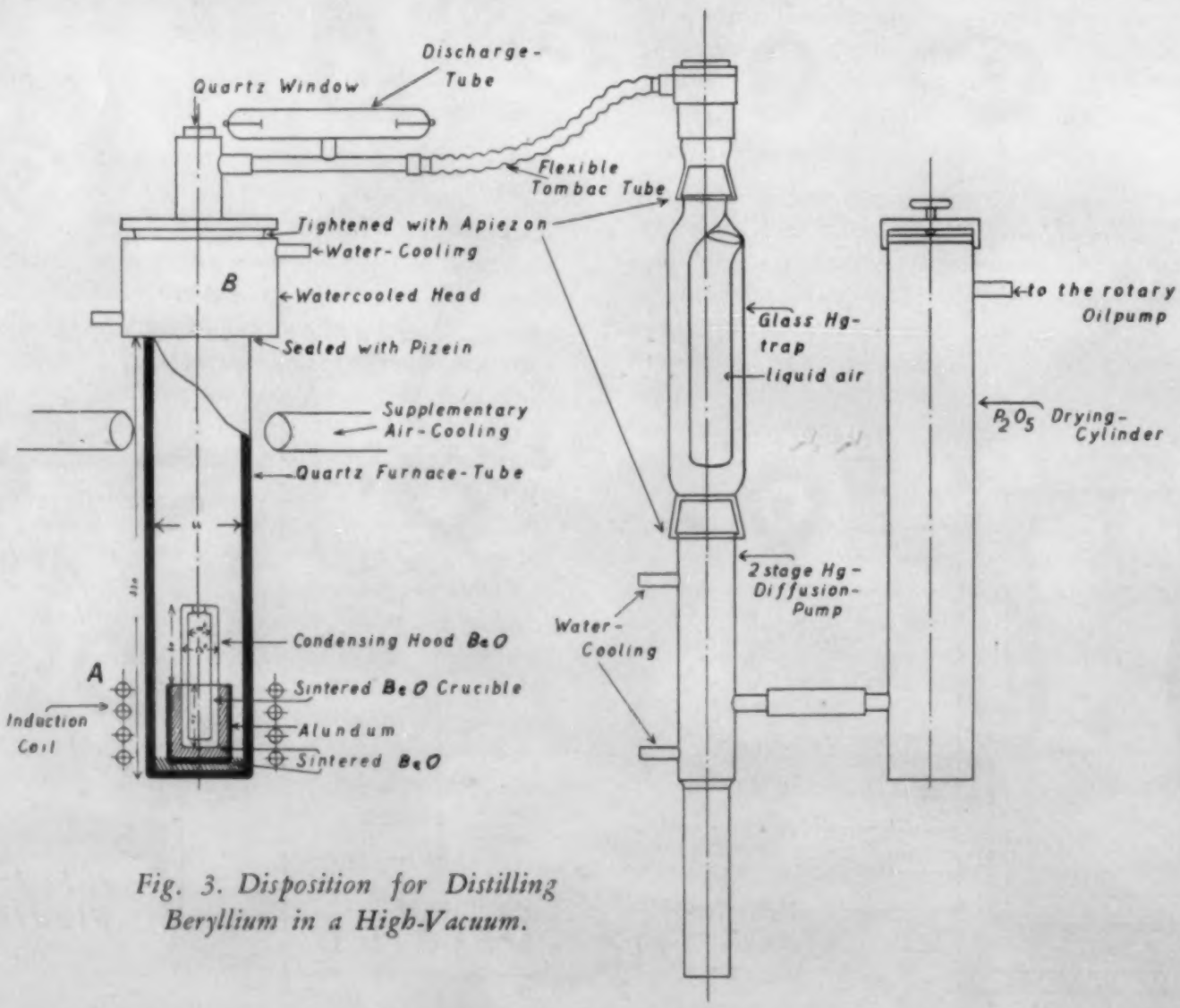


Fig. 3. Disposition for Distilling Beryllium in a High-Vacuum.

Distillate (17 g)		*Residue* (23 g.)	
Al	0.24%	Al	0.11%
Si	0.036%	Si	0.73%
Fe	trace	Fe	2.08%
Ni	nil	Ni	nil
Mn	0.38%	Mn	0.35%
Be by difference	99.344%	Be by difference	96.73%

Based on the vapor pressure curves of the pure metals, Al should enrich in the residue as it has a lower vapor pressure than beryllium. The contrary occurred. On the other hand, Mn should be enriched in the distillate, while curiously it is distributed equally in the residue and the distilled metal. This can be explained either by the uncertainty of the published vapor-pressure data, or by the abnormal behavior of the impurities in the metal. This trial proved that separation is quite satisfactory for Fe and Si, while an increase is observed in the amount of Al in the distillate, and no separation for Mn. For distillation experiments with beryllium, one, therefore, should start from a metal that does not contain these latter impurities.

In general, it is most advantageous to distil metals in an extremely good vacuum, as the vapor pressure curve has a logarithmic character, and a considerably lower temperature can be used if the pressure is below a certain "turning-point." Beryllium must be heated up to 3240 deg. T abs. at ordinary atmospheric pressure to reach the boiling point, and under these conditions no known refractory could stand either the temperature or the chemical action. It was found that at a pressure below 0.001 mm Hg, Be evaporates satisfactorily at 1400 deg. C and that at this temperature no difficulties arise from the melting point of the ceramic materials.

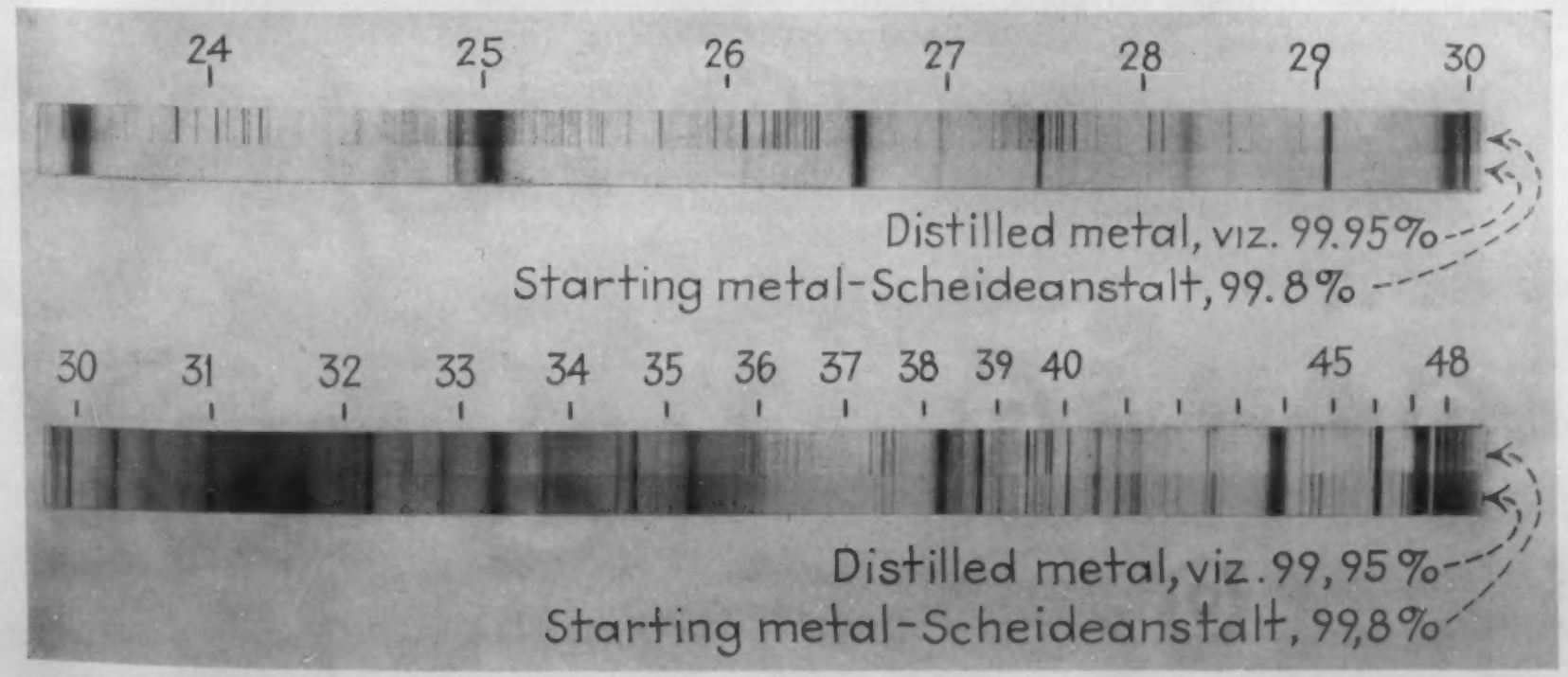
Beryllium itself reacts with all known oxides, especially in a vacuum. It can be employed for preparing Ba and Ca[10] from their oxides, a method now in use for making Ba in a good vacuum. Al is reduced readily, and beryllium even alloys with thorium and zirconium, when heating the metal in crucibles of such oxides. Therefore, due to its chemical action, only beryllia can be used as a container for melting beryllium in a vacuum. These facts were recognized by Brunner and Sloman.

Fig. 4. Pea-Size Drops of Beryllium.

Apparatus for Distillation

The apparatus used in these experiments for distilling beryllium is shown in the Figs. 1, 2 and 3. The metal is put into a crucible of sintered BeO, and this placed into a larger one of alundum with BeO-powder tamped between (Fig. 1, Detail A). Over the BeO crucible is placed a condensing hood of the same diameter, but about twice as long. An opening through the top of this hood allows control of the melting process and enables readily volatile elements to escape into the furnace tube. This whole assembly is placed in a quartz tube provided with a special head that is water cooled and tightened with pizein grease. Fig. 2 (Detail B) gives this head in more detail. Connection with the diffusion Hg-pump is made by means of a flexible tombac-tube. (Fig. 3) A discharge tube enables some control of the vacuum. A Hg-trap, cooled with liquid air, avoids contamination by mercury vapor.

Fig. 5. Compared Spectrograms of Beryllium, Starting and Distilled Metal.



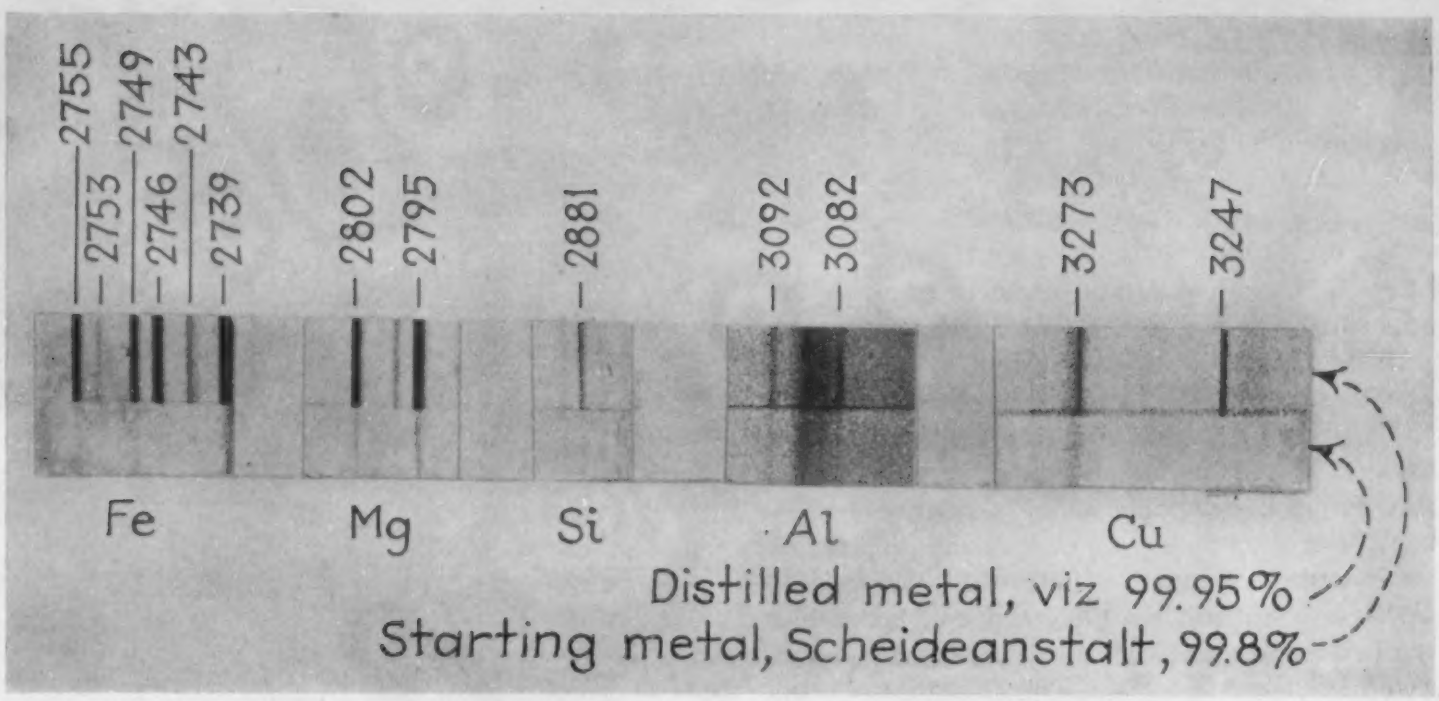


Fig. 6. Compared Spectrograms of Different Impurities in Beryllium.

If needed, supplementary cooling by means of compressed air, can be provided below the sealed head.

Melting is done by means of a high frequency induction coil that is only as high as the crucible itself, so that only a small action of eddy currents takes place in the condensed metal. One begins by melting the Be under argon without the condensing hood. The temperature is raised at least up to 1500 deg. C., so that all humidity, salts, alkaline and alkaline-earth metals are expelled. After cooling down tc about 1000 deg. C., the furnace tube is quickly opened, the condensing hood put on top of the crucible, the conical head tightened again on its seat, and pumping begun cautiously, the temperature being increased slowly. If dissolved gases are present, they escape from the molten metal with the formation of bubbles. At this moment, one must, therefore, heat with great care. The evaporation begins after the gases have been pumped off, at 1300 deg. C. The best temperature for distillation is located at about 1400 deg. C. One can observe that beryllium deposits either in the shape of drops (Fig. 4) or as a continuous film or a thick sheet. Drops are formed if the temperature of the condensing hood walls is higher than the melting point of beryllium, and if simultaneously the vapor pressure in the distilling chamber is raised to such an extent that liquid metal on the walls remains in equilibrium with the vapor. If one heats more cautiously, and if the vapor pressure of beryllium in the distilling chamber remains low, only thin films or sheets are deposited. In this case, beryllium grows as dendrites, often several centimeters long.

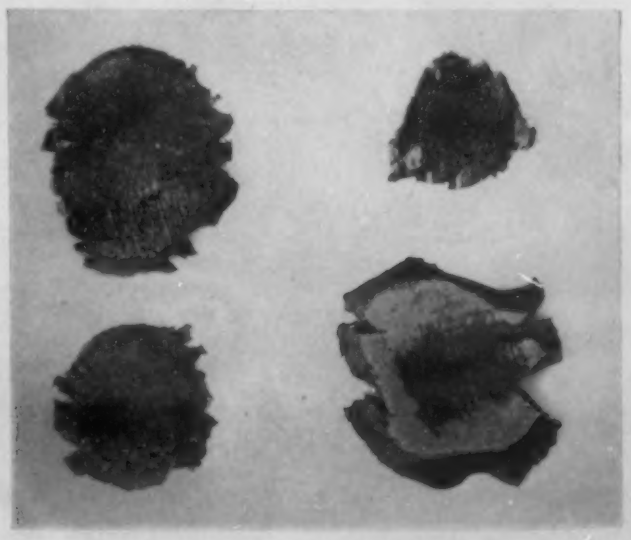
The sublimation of beryllium does not seem to be considerable, in comparison with certain metals, like Cr or Fe. It appears from this that measuring the pressure externally of the crucible itself is of little value, as one can have a pressure of a certain millimeter of beryllium vapor in the distilling chamber in the center of the condensing hood which will be quite different from that measured at the Hg-pump. The discharge tube gives a good picture of the prevailing "external pressure." If the discharges of an induction coil on the parallel spark gap reach 2 in., and simultaneously no glow is visible in the discharge tube with the electrodes 100 mm. apart, the vacuum is below 0.001 mm. Hg.

A Good Vacuum Essential

A good vacuum is essential for a rapid distillation, and a clean product. Beryllium, like all alkaline earth metals, has a strong affinity for most gases and it acts as a good

Fig. 7. Residues of Beryllium, Siemens and Halske.

Fig. 8. Distilled Beryllium of Highest Purity (99.95%) Hand-Forged.



getter for N_2 and O_2. In order to insure maintaining a high vacuum, the metal parts of the head have to be machined either from forged metal or from cast bronze impregnated with tin solder. Grinding of the conical joint has to be made with the greatest care and precision.

The purity of the distillate depends of course on the duration of the distillation, and on the quantity of metal one leaves as residue. The less volatile impurities like Cu, Fe and Si, may finally go over to a certain extent, if one prolongs the operation. It is therefore preferable to drive off only two thirds of the charge. For example, when using 25 g of raw beryllium, one can distill 15 to 17 g. without danger of contamination by Cu, Si and Fe. The residue, in this case, contains much Cu, Si, Fe, carbides, oxides and nitrides.

The best results ever obtained in the purification of beryllium came from using an especially purified metal, provided by Deutsche Gold-und Silver-Scheideanstalt, with at least 99.8 per cent Be. It was prepared from carefully chosen raw materials, and contained only 0.1 per cent of Cu + Si + Fe + Al and 0.1 per cent BeO (See spectrograms (Figs. 5 and 6). Mn and Ni were completely absent. The two kinds of commercial beryllium, which may be employed, are either prepared by the Stock-Goldschmidt method in a fluoride bath (Siemens & Halske) or by the chloride electrolysis (Beryllium Corp. and Deutsche Gold-und Silberscheideanstalt). The commercial metals resulting from both processes differ in respect to their impurities. The first, in general, has more carbides and Mn, while the latter often contains much Al, but is free from Mn. Therefore, the first gives a distilling residue like that of Fig. 7, due to the very sluggish bath. (See carbides.) The separation of Al from the raw materials of the chloride electrolysis is not easy, and it is this impurity, especially, that cannot be eliminated by the distillation process.

A chemical analysis of the obtained distillation products has been given above. At high purity, only spectrographic methods enable getting reliable data with small samples. Therefore, control was perfected only by means of the spectrograph in the case of high purity beryllium, 99.8 per cent. The Figs. 5 and 6, give a comparison of the spectra of the essential impurities in the raw material 99.8 per cent and in the distillate. It can be seen that the purification was exceedingly good. Almost all the iron disappeared. An improvement can be observed in the Al content, and Cu and Si are barely traceable. This distilled metal has been forged after being heated by an acetylene-oxygen blow-pipe. Fig. 8 shows that it is malleable, but some cracks appear on the corners. The hardness found in this beryllium, that certainly reaches 99.95 per cent purity, was 111 Brinell at 187.5 kg. load, 2.5 mm. ball, 1 minute. The metal was in the slowly cooled condition. Comparison with an Al, Hoopes, 99.9973 per cent proved that this metal had a similar degree of purity.

At the present time, we have ignored which elements are obnoxious to the ductility of beryllium. Sloman supposes that apart from Fe, Si and carbides, oxygen may interfere. He therefore condensed his metal on a water-cooled quartz hood. There is no indication that this supposition is right or wrong, but if BeO makes beryllium brittle, we would not, in the future, expect to see beryllium sheets or wire on the market, the only non-reacting ceramic material for melting and distilling beryllium being beryllium oxide.

Fig. 9. Distilled Beryllium, Lower Grade, Hot Rolled, Strained 15 to 20 x 0.5 to 0.7 mm. thick.

Due to the cost of the refined 99.8 per cent raw material, other trials were conducted with a commercial beryllium (Deutsche Gold-und Silberscheideanstalt) 99.5 per cent the remainder being essentially Fe and Al. The distilled metal, in the shape of small drops, was heated in a $BaCl_2/CaCl_2$ (25/75 per cent) bath to a temperature of about 800 deg. C. by plunging it below the salt surface with tongs. It was carefully rolled and appeared to be, to a certain extent, malleable. Fig. 9 shows the resulting sheets, 0.5 and 0.7 mm. thick. After cogging, further rolling is quite easy. It seems that first the rough crystal structure has to be broken up and, after this, rolling proceeds quite well. Cracks occur regularly at the beginning, but only along certain crystal surfaces on the borders. Therefore, it seems that in the future the metal may have to be remelted under a noble gas, and poured in an iron mold to produce a finer grain in attempting to get a more readily rollable material. The sheets are brittle as cold, even after annealing. Their whole behavior resembles a great deal that of rolled Cr or Bi. Although, this is a serious obstacle to the use of pure beryllium as an engineering material, it is possible there will be growing interest in the metal for specialized uses, such as in X-ray work for windows and filters.

Conclusions

Very pure beryllium refined by distillation in a good vacuum and condensed on beryllium oxide is to some extent malleable when hot. Sheets could also be prepared from a less pure distilled metal by hot rolling. They show cracks on the corners, and are quite brittle as cold. Cold brittleness appears to be a physical property of the element.

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Courtesy: Bethlehem Steel Co.

A Heavy Forging Operation

A CORRELATED ABSTRACT ON

Corrosion and Corrosion-Resistant METALS AND ALLOYS

by V. V. Kendall

Section Editor, Current Metallurgical Abstracts of METALS AND ALLOYS.

This is the second installment of the author's correlated abstract of papers delivered at important symposiums during 1936. The first appeared in the November issue which covered ferrous products. This one reviews non-ferrous metals and alloys. The symposiums included in the entire abstract are described in the first installment and should be consulted. The references list the papers from the different symposiums as abstracted.

Nickel and Its Alloys

The papers by Geiger[30], McKay[31] and LaQue[32] give a wealth of data on nickel and nickel-base alloys. Moreover these are readily available so only an outline of recent developments will be given. Nickel and its alloys fall in the five groups: (1) pure nickel, including nickel-clad steel; (2) Monel, including regular Monel, K-Monel, that can be hardened by heat treatment; and two special varieties of cast Monel having extra hardness, and known as grades H and S; (3) Inconel, including Inconel-clad steel; (4) the Hastelloys A, C, and D; and (5) Illium.

In considering the various corrosive media, McKay and Worthington ("Corrosion Resistance of Metals and Alloys, 1936) divide them into 10 groups: Air, soil, acids, oxidizing agents, natural waters, salts and brines, organic materials and foods, high temperatures, sulphur compounds, and alkalies. Furthermore, using the measure of corrosion rate—mg./sq.dm./day—he divides this value into the following ranges:

> Rates below 10 are so small as to be usually harmless.
>
> From 10 to 100, rates become appreciable and in the neighborhood of 100, they need careful consideration.
>
> From 100 to 500, corrosion is serious, and figures above 500 usually indicate unsuitability.

This is the first attempt to transfer quantitative corrosion data into terms that mean something in economic life. It affords a very valuable yardstick. For instance, nickel is rated as follows:

Fig. 1.—Pure Nickel Reaction Kettle Used in the Manufacture o Phenolic Resin. (Courtesy: International Nickel Co.)

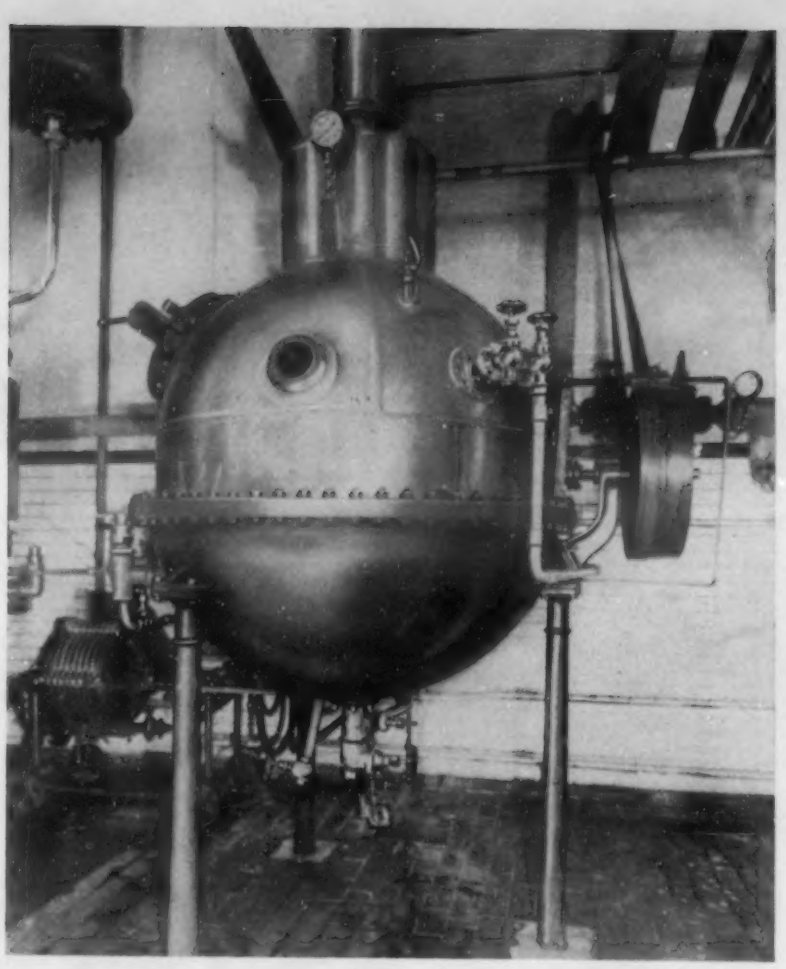
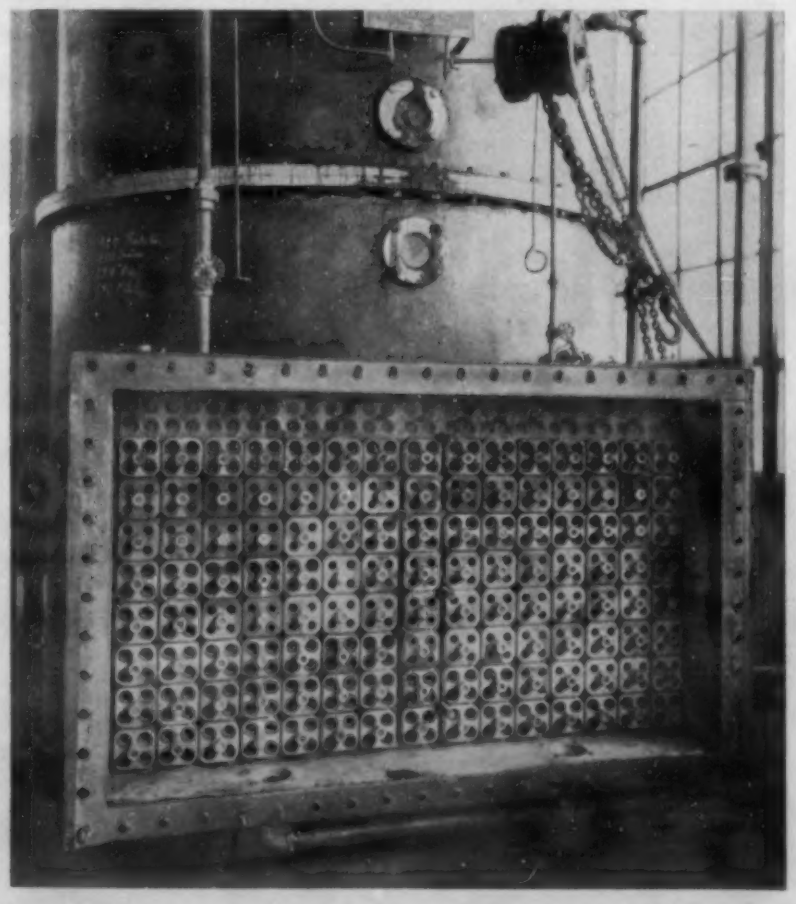


Fig. 2.—Inconel Vessel Used in the Preparation of Food Extract. (Courtesy: International Nickel Co.)

Strong acid	10 —	200
Weak acid	10 —	60
Oxidizing acid	1,000 —	10,000
Caustic alkali	0 —	1
Fresh water	0 —	1
Salt water	0 —	6
Ordinary atmosphere	1 —	2

Fig. 3.—Evaporator Equipped with Monel Tubes for Concentrating Zinc Chloride. (Courtesy: International Nickel Co.)



Of the 10 groups, six—air, soil, acids, oxidizing agents, natural waters, salts and brines, organic materials and foods, and alkalies are well resisted by nickel. Three others are reasonably well resisted. In acids where oxidizing agents are present, corrosion may be quite rapid. In high temperatures, nickel forms a protective scale whenever oxygen is present and is not otherwise readily acted upon except by sulphur compounds. Sulphur, aside from sulphates, is active on nickel both in acid solutions and at high temperatures. For special applications nickel-clad steel has been quite successful. A nickel layer, usually 10 per cent of the total thickness of the plate or sheet is bonded to the steel so that the final product can be rolled into plates or sheets. It is easily joined by welding.

Monel metal, which is a so-called natural alloy of 68 per cent Ni, 29 per cent Cu, is the most widely used of the nickel alloys. Monel probably possesses a useful resistance to a greater number of corrosive media than any other metal. The latest development in the Monel alloy is the addition of 3.5 per cent aluminum to produce K-Monel and the addition of 2.75 and 3.75 per cent Si to produce H- and S-Monel, the H and S being available only in the cast form.

The K-Monel is a precipitation-hardening alloy which, from the standpoint of resistance to corrosion is approximately the same as regular Monel. Cold-drawn K-Monel in the form of rods can be made with breaking strengths as high as 165,000 lbs. per sq. in. and hard-drawn spring wire as high as 175,000 to 200,000 lbs. The corrosion resistance of the Monels differs in degree only and they can be considered as a group, the use of a specific Monel depending upon physical properties rather than corrosion resistance.

Inconel was introduced in 1931 and has the composition 79-13-7 Ni-Cr-Fe. It was developed primarily to resist corrosion and tarnishing by foods, especially dairy products and fruit juices, for which it is excellent. At the same time its composition is such as to make it resistant to a great variety of corrosives, and its more general use in industry is increasing rapidly. In strongly oxidizing acid solutions, Inconel is practically free from attack. However, the oxidizing effect of dissolved air alone is not sufficient to insure complete passivity and freedom from attack by air-saturated mineral acids or concentrated organic acids. The high nickel content provides excellent resistance to corrosion by alkaline solutions. There are also a number of alloys available containing from 60 to 80 per cent nickel and from 13 to 20 per cent chromium with the remainder mostly iron, which are used principally for heat-resisting purposes. In general, their corrosion-resisting characteristics are similar to those of Inconel.

The Hastelloys were developed for specific purposes. Hastelloy A (58-20-20-2 Ni-Fe-Mo-Mn) was developed primarily as a material to resist corrosion by hydrochloric acid. Hastelloy C (58-6-14-17-5 Ni-Fe-Cr-Mo-W), which is available only in cast form, possesses an unusual degree of resistance to oxidizing solutions, especially those containing chlorides, in addition to other corrosive chemicals. It is very resistant to hypochlorite solutions and moist chlorine. Hastelloy D (85-3-2-10 Ni-Cu-Al-Si), also available only in cast form, is resistant to all concentrations of sulphuric acid at temperatures up to the boiling point.

Illium (56-8-24-4-1-1.5-2 Ni-Cu-Cr-Mo-Si-Mn-W),

available only in cast form, was developed as the result of a search for a material resistant to both sulphuric and nitric acids over a wide range of concentration and exposure conditions. It is superior in applications under highly oxidizing conditions, such as nitric acid, and has limited applications in hydrochloric acid and acid chlorides.

Another recent development is the corrosion-resistant, hard surfacing material known as Colmonoy[32]. The No. 6 grade has a nickel base of about 75 per cent. Another essential constituent is chromium boride. This material produces deposits having a hardness of 58 to 60 Rockwell C (545-575 Brinell) and the deposits are resistant to mineral and organic acids and to alkalies. The coating material may be deposited by oxyacetylene or metallic arc welding, or may be cast on by pouring the molten alloy at from 2350 to 2500 deg. F. into a suitable mold containing the base metal preheated to from 1200 to 1400 deg. F. Colmonoy No. 6 is used for pump sleeves, pump rods, cam collars, etc., and for plug cocks to counteract galling or seizing tendencies.

The physical properties are liberally covered in tables. In particular the papers of Geiger[30] and the second part of LaQue[32] on the heat treatment, machining, and welding of Monel, nickel, Inconel, and Hastelloy.

Aluminum and Its Alloys

Resistance to corrosion, lightness, and strength are the properties that have been responsible for the growth of aluminum and its alloys and also magnesium. The resistance to corrosion of aluminum and aluminum alloys is largely the result of their film-forming characteristics. An excellent summary of the corrosion resistance of aluminum and aluminum alloys is given by Dix and Mears[39] as follows:

1. *Atmospheric Exposure:* Pure aluminum or the resistant aluminum alloys are little affected by even rather long periods of exposure to the atmosphere in a wide range of different locations. If it is desirable that a bright surface be maintained, the alloy should generally be Alumilited.

2. *Marine Exposures:* The Alclad aluminum alloys and 52S and 53S are highly resistant to sea water or salt spray.

3. *Neutral Salt Solutions:* Aluminum and many of its alloys are little affected by solutions of most neutral salts. The halogen salts are more active so that special precautions must sometimes be taken if aluminum is to be used in direct contact with their solutions.

4. *Alkaline-Salt Solutions:* Aluminum is generally attacked by alkaline salt-solutions. This attack can be inhibited by the addition of sodium silicate.

5. *Acid-Salt Solutions:* Solutions of salts of the heavy metals having an acid reaction are generally quite corrosive to aluminum. This is especially true for the halogen salts. Oxidizing acid salts, such as potassium dichromate, generally do not attack aluminum.

6. *Mineral Acids:* Either very dilute or very concentrated nitric or sulphuric acids have little effect on aluminum. Intermediate concentrations are quite corrosive. Sulphurous acid attacks aluminum only slowly at concentrations up to 1 normal. Boric acid has very little action on aluminum, even up to saturated solutions. However, the halogen acids are quite corrosive.

7. *Organic Acids:* Most organic acids do not have much effect on aluminum unless they are almost devoid of water. However, formic, oxalic, and mono- and tri-chlor acetic acids are rather corrosive.

8. *Alkalies:* Sodium- and potassium-hydroxide solutions readily attack aluminum at all but the lowest concentrations. Ammonium hydroxide does not seriously attack aluminum.

9. *Organic Solvents:* Aluminum is not appreciably attacked by a wide range of organic liquids. However, some, e.g., the alcohols, do attack aluminum if completely anhydrous.

10. *Gases:* Dry gases are generally inert to aluminum. Many moist gases such as ammonia and hydrogen sulphide also have little effect on aluminum while some other moist gases have slight action. Moist chlorine is decidedly corrosive.

The demand for corrosion resistance and strength combined with lightness, as exemplified in the aircraft industry has furnished a logical outlet for aluminum alloys and we find the duralumin type alloy 17 S-T (4 — 0.5 — 0.5 Cu — Mn — Mg) as the standard for this purpose. The 24S alloy (4.2 — 0.5 — 1.5 Cu-Mn-Mg), however was later developed for higher strength and is superseding alloy 17S in aircraft work but not in other fields.[35]

Fig. 4.—Eros, an Aluminum Statue, Has Been Exposed to the Fog and Grime of London since 1893. An examination about a year ago disclosed the fact that it was in excellent condition and unaffected by industrial atmosphere. (Courtesy: Aluminum Co. of America.)

There has been considerable development in recent years of coatings, particularly of metallic coatings of the nature of Alclad, nickel-clad, etc. The use of such metal coatings removes the necessity of painting, which is an advantage, varying with the application of the material. The aircraft industry has offered an almost made-to-order market for aluminum alloys and much use has been made of Alclad for that purpose.

The other aluminum alloys have not suffered in their application to other industries, however. The addition of a small amount of chromium to 51S (1 — 0.6 — 0.25 Si-Mg-Cr) has improved that alloy for forging. The common wrought alloys contain varying amounts of manganese, magnesium and chromium.

Table V.—Typical Physical Properties of Copper and Its Alloys

Material	Tensile strength, lb. per sq. in. Hard	Tensile strength, lb. per sq. in. Soft	Elastic limit, lb. per sq. in. Hard	Elastic limit, lb. per sq. in. Soft	Elongation, per cent Hard	Elongation, per cent Soft	Rockwell B hardness Hard	Rockwell B hardness Soft	Melting point, C.	Density, lb. per cu. in.	Coefficient of expansion	Electrical conductivity[1]	Thermal conductivity[2]	Modulus of elasticity, lb. per sq. in.
Coppers:														
Electrolytic copper..	55,000	30,000	50,000	0	5	50	95[3]	20[3]	1083*a*	0.322	0.0000177*e*	101.0	0.923*e*	16×10^6
Phosphorized copper.	58,000	34,000	55,000	0	5	50	98[3]	23[3]	1083	0.322	0.0000177	74.7*d*	0.727*d*	16×10^6
Arsenical copper.....	60,000	35,000	56,000	6,000	5	45	98[3]	23[3]	1083	0.322	0.0000177	50.0*e*	0.398*e*	16×10^6
Argentiferous copper (4 to 12 oz. silver per ton)	55,000	30,000	50,000	0	5	50	95	20	1083	0.322	0.0000177	101 *d*	0.923*e*	16×10^6
Brasses[e]:														
Red brass (85 Cu, 15 Zn)..	89,000	45,000	85,000	15,000	4.5	43	89	3	1020	0.316	0.0000187	37.0	0.38	15×10^6
70-30 Brass (70 Cu, 30 Zn)..	95,000	53,000	91,000	16,000	7	51	93	15	955	0.308	0.0000199	27.58	0.290	15×10^6
High brass (65 Cu, 35 Zn)..	93,000	51,000	73,700	18,500	2	50	90	30	930	0.306	0.0000202	26.8	0.285	15×10^6
Admiralty (71 Cu, 28 Zn, 1 Sn)	100,000	53,000	98,000	18,000	4	67	95	15	935	0.308	0.0000202	24.65	0.263	15×10^6
Aluminum brass (76 Cu, 22 Zn, 2 Al)	83,000	62,000	75,000	16,000	5	52	86	33	970	0.301	0.0000185	22.56	0.240	15×10^6
Muntz metal (60 Cu, 40 Zn)...	88,000	59,000	82,000	15,000	5	52	91	24	905	0.304	0.0000208	28.60	0.300	15×10^6
Commercial bronze (90 Cu, 10 Zn)...	67,000	37,600	55,000	15,000	3	40	75	1	1045	0.318	0.0000182	40.90	0.446	15×10^6
Roman or Tobin bronze (60 Cu, 39.25 Zn, 0.75 Sn)	90,000	54,000	70,000	15,000	4	40	93	55	885	0.304	0.0000211	24.93	0.279	15×10^6
Bronzes[e]:														
5 Per cent phosphor bronze ..... (95 Cu, 5 Sn, 0.05 P)	105,000	51,000	85,000	15,000	7	55	91	30	1050	0.320	0.0000178	18	0.20	15×10^6
8 Per cent phosphor bronze ..... (92 Cu, 8 Sn, 0.05P)	110,000	55,000	90,000	15,000	3	60	99	38	1030	0.319	0.0000182	13.61	0.154	14×10^6
10 Per cent phosphor bronze ..... (89.5 Cu, 10.5 Sn)	115,000	60,000	95,000	16,000	5	65	100	52	1000	0.317	0.0000183	10.6	0.121	15×10^6
Aluminum bronze... (92 Cu, 8 Al)	134,000	76,000	110,000	30,000	13	55	99	69	1060	0.293	0.0000165	15.23	0.173	15×10^6
Silicon bronze, type A	120,000	67,000	103,000	24,000	10	60	99	65	1000	0.308	0.000017	8.07	0.086	
Silicon bronze, type B	90,000	42,000	80,000	12,000	10	60	84	20	1030	0.313	0.000017	11.0	0.116	
Copper-Nickel Alloys[e]:														
Cupronickel ..... (80 Cu, 20 Ni)	80,000	49,000	75,000	18,000	3	42	87	21	1200	0.321	0.0000159	6.47	0.087	17.0
Cupronickel ..... (70 Cu, 30 Ni)	84,000	49,000	80,000	18,000	4	50	87	20	1220	0.323	0.0000162	4.75	0.093	17.0
20 Per cent nickel silver ..... (70 Cu, 10 Zn, 20 Ni)	81,000	49,500	78,000	16,500	5	44	86	12	1150	0.321	0.0000164	4.8	0.069	18.0
18 Per cent nickel silver ..... (64 Cu, 18 Ni, 18 Zn)	100,000	54,500	80,000	18,000	5.5	42	94.5	40	1110	0.316	.....	5.91	0.080	18.0
10 Per cent nickel silver ..... (65 Cu, 25 Zn, 10 Ni)	90,000	50,000	75,000	18,000	3	45	90	52	1010	0.313	.....	8.27	0.110	17.5

[1] Per cent of International Annealed Copper Standard.

[2] Cal. per sq. cm. per cm. per sec. per C. at 20 C.

[3] Hardness numbers for the coppers is in Rockwell F; all others, Rockwell B.

a Circular No. 73, U. S. Bureau of Standards.

b Scientific Paper No. 410, U. S. Bureau of Standards.

c "Arsenical and Argentiferous Copper," J. L. Gregg.

d "Thermal and Electrical Conductivities of Copper Alloys," C. S. Smith and E. W. Palmer, A.I.M.E. Tech., Bull. No. 648, 1935.

e Data based on information published by Revere Copper & Brass, Inc., American Brass Co., and Chase Brass & Copper Co.

Reviews of the many aluminum alloys are given by Dix and Bowman[35], Fink[36], Dix and Mears[39]. The structural factors to be considered in their application to structural design are covered by Jeffries, Nagel and Wood[37], Hartmann[38] and Winston.[40] Röhrig[32] discusses the application, handling, cleaning, etc. of aluminum. The anodic oxidation of aluminum and its industrial application is also discussed by Miyata[34]. The magnesium alloys are rapidly coming to the front in aircraft and structural applications and further decrease in production costs should result in their extended use.[40]

Copper and Its Alloys

Copper and its alloys have been discussed by Davis, [41] Crampton[42], and Wilkins.[44] Wilkins gives a review of 117 references. Although not in the symposium but of considerable interest is the article of Silliman[43] on the beryllium-copper alloys. Beryllium-copper, which contains from 2.0 to 2.25 per cent Be, when quenched from about 800 deg. C. produces a ductile, malleable structure which can be cold-worked by commercial practices such as rolling, drawing, swaging, pressing, etc. It can be hot-worked at temperatures below about 775 deg. and above 575 deg. Reheating after forming hardens and strengthens the alloy. It is used for springs or for articles requiring high corrosion resistance, high resistance to fatigue and high resilience.

Typical physical properties of the coppers and copper alloys are given in Table V. Some of the more recent developments can be noted. Aluminum brasses have shown remarkable resistance to impingement type of attack but, under certain conditions, are subject to dezincification. The addition of tin has corrected this tendency. The following figures[42] which are the result of water-line

tests carried out on a number of samples of each alloy, using dilute sea water for 100 days at 60 deg. C., illustrate this fact:

Cu %	Al %	Sn %	Zn %	Original strength lost by corrosion	Original elongation lost by corrosion	Type of attack
70	..	1	29	6	25	Layer type dezincification
76	2	..	22	45	79	Plug type dezincification
80	2	1	17	1	14	General thinning

Arsenic has been added to brasses to prevent dezincification but such brasses are subject to intercrystalline attack. The addition of antimony shows no such tendency.[42] The data below are the result of water-line tests conducted in a solution of 0.5 per cent sodium chloride and 0.5 per cent malic acid at 60 deg. C. for 30 days:

Cu %	Sb %	Original tensile strength lost by corrosion	Original elongation lost by corrosion	Type of attack
65	....	42	68	Layer type dezincification
	0.007	8	19	Layer type dezincification
	0.02	5	15	General thinning
	0.09	4	16	General thinning
70	....	45	77	Plug type dezincification
	0.06	5	9	General thinning
75	....	30	62	Layer type dezincification
	0.06	3	3	General thinning

The nickel-aluminum bronzes are relatively new. The precipitation hardening type is particularly useful. Two such alloys are available.[42] One contains about 91 per cent Cu, 7.5 per cent Ni and 1.5 per cent Al, and the other 82 per cent Cu, 15 per cent Ni and 3 per cent Al. The first alloy can be extensively worked either hot or cold and is also capable of considerable precipitation hardening. It finds application in propeller shafts and similar structures where a hard, high-strength, tough, corrosion-resistant alloy is necessary. The second alloy is readily hot-worked but can be cold-worked relatively little and then only with difficulty. It is hard and strong and is quite susceptible to precipitation-hardening treatment. It finds application to parts of such size and form as to lend themselves to fabrication hot and where a material is desired with great strength, hardness, abrasion resistance, and corrosion resistance, along with ability to be age-hardened.

A unique recent development has been the production of composite tubes to be used as condenser or heat exchanger tubes in oil refineries.[42] These tubes are commercial bronze on the side exposed to water and admiralty brass on the side exposed to oil. There is only a slight difference in the coefficient of thermal expansion and, in production, no particular annealing, pickling or scrap disposal problems arise.

An important innovation in the welding field is that of non-fuming brazing rod. The addition of either beryllium or silicon to Muntz metal type brazing rod suppresses the zinc fume produced when brazing with the old type rod.

Lead

The properties of lead, with data on corrosion resistance, are given by Hiers.[45, 47] Recent developments have extended the uses of this age-old metal very considerably. A new type of chemical lead containing 0.04-0.08 per cent Cu and also 0.02 per cent Bi has been produced which is said to possess some advantages in mechanical properties over standard chemical lead.

Tellurium lead (0.05% Te) is the most important development in the lead field. It has unusual resistance to hot concentrated sulphuric acid, has a higher fatigue limit

Fig. 5.—Aluminum Scoops and Shovels are Beginning to be Used Exclusively in Industries Where it is Imperative that the Metal Does Not Attack the Product and Vice Versa. (Courtesy: Aluminum Co. of America.)

Fig. 6.—A Five-Sided Fuel Tank of Herculoy for Diesel Coast Guard Boats. (Courtesy: Revere Copper and Brass, Inc.)

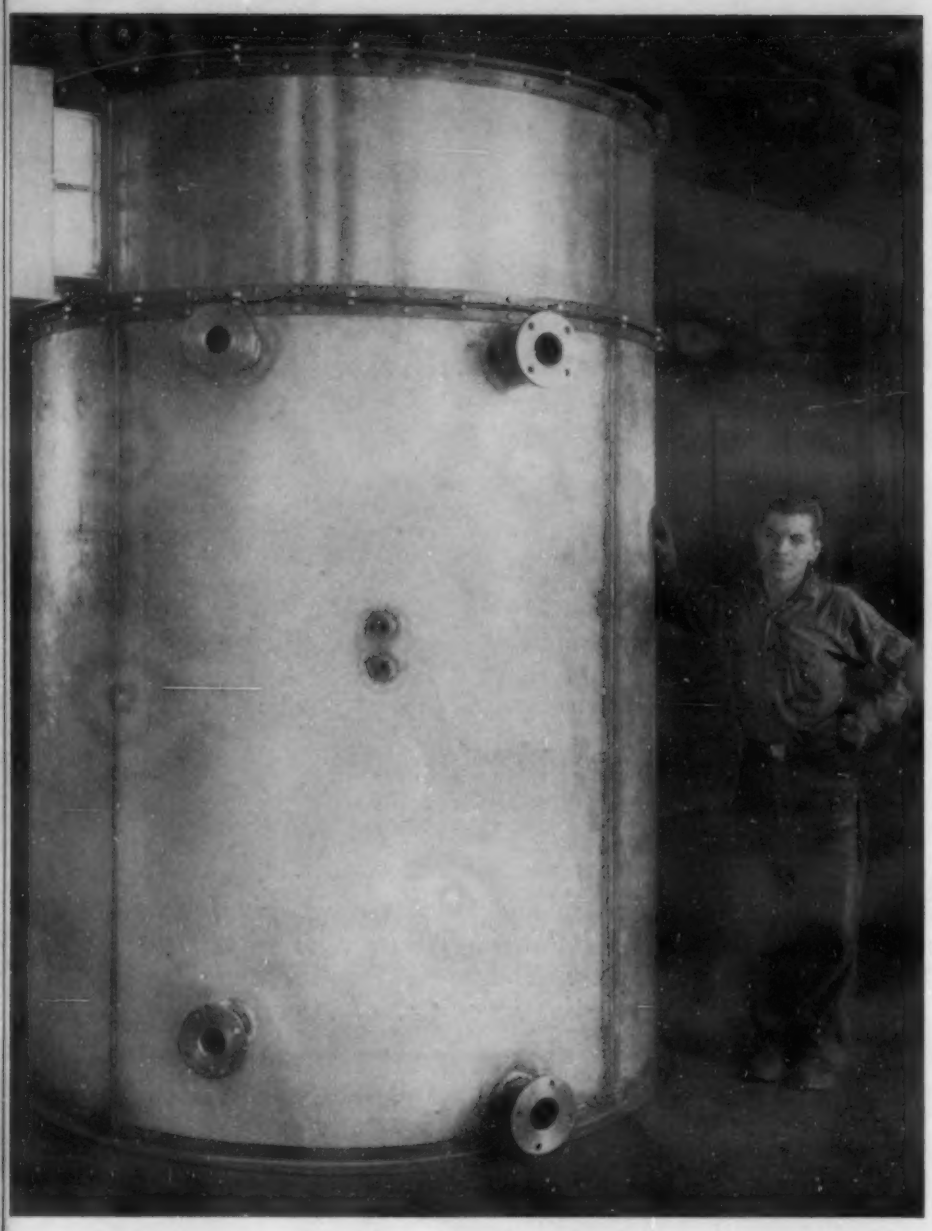


Fig. 7.—A Herculoy Tank for the Water System of the Library of Congress. The lower section is 7 ft. high and 6 ft. in diameter. The tank is lined with block tin. (Courtesy: Revere Copper and Brass, Inc.)

than pure lead, and can be work-hardened. The addition of tin, antimony and cadmium to lead has received some consideration in England but they have not found application in this country. Higher tensile strength is obtained but corrosion resistance does not seemed to be improved.

The addition of calcium to bearing alloys has been a decided improvement. For telephone cable sheathing, 0.03 to 0.04 per cent Ca has resulted in an alloy of higher strength and a relatively high endurance limit with a corrosion resistance equal to that of the lead or the 1 per cent antimonial lead frequently used as cable sheathing. For chromium plating tanks, a 7 per cent Sn-93 per cent Pb alloy is recommended. In the production of high-purity commercial zinc (99.97%), it has been found that the addition of 1 per cent silver to lead forms an insoluble anode.

Zinc

The position of zinc in the world of metals has been that of a protector of steel and its use for this purpose is reviewed by Anderson.[46] Pure zinc sheet when strengthened by the addition of small amounts of cadmium, copper and magnesium, is now being marketed in the form of corrugated roofing sheet.[47] A new type of zinc-coated steel wire has been recently developed. The coating, consisting of electro-deposited high-purity zinc, is applied and then the wire is treated mechanically to give it a uniform and smooth surface. This product is expected to be more serviceable than ordinary galvanized iron or steel wire.

Silver

Considerably more silver equipment is produced than is generally realized. Certain chemicals require processing in silver. The production of phenol requires the use of a large amount of silver. The food industries, the photographic industry and the acetate division of the rayon industry are all examples of the use of silver. The applications of silver, gold, platinum and tantalum are discussed by Lee.[48]

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A Few Chuckles

The "Body" of Steel

This is an untouched micrograph, at a magnification of 1000 diameters, of a tiny area observed by J. R. Vilella, of the United States Steel Research Laboratory, Kearny, N. J., in the course of an examination of a polished and etched section of a piece of steel.

This picture should strengthen belief in the substantiality of the

"body" of steel, or of some part of it, at least. It also looks something like a French postage stamp, and so suggests "timbre." Some may prefer to regard the figure as being that fickle goddess, the spirit of steel. She is clearly a high-brow and has, like the S-curve, a distinctive nose, but is, like justice, apparently blind, all of which has inclined us to call her NO-SEE. This, we are unreliably informed, is the term anciently used in some parts of China to designate this essential attribute of steel, hitherto so elusive. It is a fine, though not unusual, example of a name which emphasizes the more significant aspects of the subject by directing attention towards features which are absent or largely irrelevant and anthropomorphous.—JOHN JOHNSTON.

"Spanish Metallurgical Progress"!

The following clipping from the Oct. 15, 1937, issue of the *Baltimore Evening Sun,* illustrates Spanish ordnance metallurgical progress! It was titled "Franco Uses Shell That Melts Steel."

> London, Oct. 15 (AP)—A new German shell that melts iron and steel is being used by Franco's forces, says Prince Hubertus Loewenstein, the German author, who recently returned from Republican Spain.
>
> "The shells, with a specially prepared *termite* filling, are fired by ordinary anti-tank guns. Exploding inside the tank, they develop a heat of 4,000 degrees Centigrade, by which, of course, steel and iron melt like snow," Prince Hubertus said. (Italics supplied.)

A. P. CALVERT, Lieut., U.S.N.
Naval Eng. Exp. Station, Annapolis, Md.

That Hungarian Postcard!

The Hungarian postcard shown on page 220 of the August issue of METALS AND ALLOYS was deciphered by about a dozen readers. Instead of calling us to account for some sin of omission or commission, it turns out to be an admonition to enlarge our best snapshots! Some readers indicate that the card was probably copied from some "ad." and not by a native Hungarian, possibly by a spoofingly inclined tourist. The signature has been given by the various translators as "Manu Porpria," "J. E. Marossy," "J. J. a Hny," "F. Jeno Foldy," "J. K. Harry," "Jean Dobozy," "F. J. Dony' and "*;#„(*—1¾=$"&) ouch!!

We insist that, should anybody want to call us a son of something in Hungarian, hereafter he sign his name in English.—H.W.G.

Two translators, who sent in their replies practically simultaneously, were awarded subscriptions. They were Julius D. Madaras, Madaras Motor Power Corp., Detroit, and Olga Zeiger, The Wm. D. Gibson Co., Chicago. The translators all sent in practically the same interpretation, except of course the signature.—Editor.

Of Interest to the High Temperature Metallurgists!

The cartoon, here reproduced, suggests that perhaps even "artists" and "Collier's" are getting high temperature minded.—N. L. Mochel.

"We musta let it hang out in the sun too long."

[The cartoon is reproduced by permission of Collier's. The artist is Reamer Keller.—Editor.]

Fact? and Fiction

"Sooner or later some part, crystallized by long use, would snap, and then * * * *," Deep Harbor, by J. Hawkins, *Colliers*, Nov. 4, 1937, p. 56.

"Buick connecting rods have a new non-crystallizing babbitt," A. M. Wolf, *S.A.E. Journal*, Nov. 1937, p. 495.

We can stand it in a piece of fiction, for one doesn't expect non-technical editors to bother about technical precision, but it becomes something more than amusing when a technical journal uses the terminology of the garage mechanic.—H.W.G.

Hardening Steel

F.G., PORTLAND, ORE. An easy method for hardening a piece of steel consists of immersing the metal in a tank of boiling linseed oil to which rosin has been added in the proportion of one eighth of a pound to a gallon of the oil. When the steel has reached the same temperature as the oil, remove it, dust it over with powdered rosin, and then plunge it into cold kerosene. From *Popular Science* for October.—C. S. MOODY, Northwest Engineering Corp., Green Bay, Wis.

Letters to the Editor

Research

To the Editor: The editorial "Research" in the August issue like most of the editorials in METALS AND ALLOYS, was read with a great deal of interest. The second paragraph, however, was read and reread with mixed feelings and calls for some comment—not so much from the view of a sin of commission but rather, in the mind of one consultant, of omission.

The last word is often that which creates the more lasting impression in the eyes of the reader, the impression in this case being that, first, research pays—which it does—when properly planned and carried out (incidentally, thanks for the boost) but second, that the small company not organized for research must turn to the richly endowed institution. Why?

These institutions serve a useful purpose of course. They have notable successes to their credit. Who would deny it? They have, it is true, fancy apparatus and marble columns and some equipment not available elsewhere. They have, some of them, unusually efficient press agents and even news departments, and they get plenty of press releases and free advertising. (Which is more than the ordinary commercial or independent research laboratory gets; or at times wants, if the truth is known.)

But why not give equal publicity to the accepted fact that there are efficient and independent consultants and research laboratories, known perhaps more commonly as "commercial testing" laboratories. Industry in part knows it and large industrial organizations are perhaps more aware of the value and functions of the independent laboratory than are the small companies in general. The largest ones must know it; they are the first to use the services of such consultants and laboratories.

It is true that the independent and unendowed or non-tax supported and private laboratory does not get into the news so much, but that is quite natural, for in many cases the work or service is confidential in whole or in part and confidences must be preserved. On the contrary, one might find it hard to defend a policy of reticence as to procedure or results on the part of a research institution supported to any extent by taxes or public funds of whatever sort. Not all, of course, are of that type, though most are tax exempt, which is more than our group can say!

Not all the inconsistency is in Washington. Some of the strongest opponents of socialization of industry are, by default at least, proponents of the socialization of the professions. Perhaps the writer will be forgiven, however, for suggesting that *there are* conscientious, well-staffed, efficient and independent but private consulting and research laboratories; that there is a place for such an independent research group in the sun and that more small industrial companies, as well as the large ones, might do worse than turn to them for help in initiating, developing and installing new processes. There is a place for the endowed institution and there is one for the private self-supported research laboratory. But give the latter a break. Of the two groups they have been and must apparently remain, the less articulate.

THOMAS A. WRIGHT.

New York.

Rapid Malleableizing

To the Editor: In reference to the note on "Rapid Malleableizing" in the High Lights in the September issue of METALS AND ALLOYS, apparently neither the Russian workers nor the commentator is aware of the fact that the processes they are describing is the subject of an American patent No. 1,688,438 granted in 1928 and that its mechanism was discussed before the then A.S.S.T. at the Cleveland meeting in 1929.

I do not know whether the joke is on me, on Saito and Sawamura who discovered the process in Japan at the same time that we did here, the Russians, or the METALS AND ALLOYS commentator.

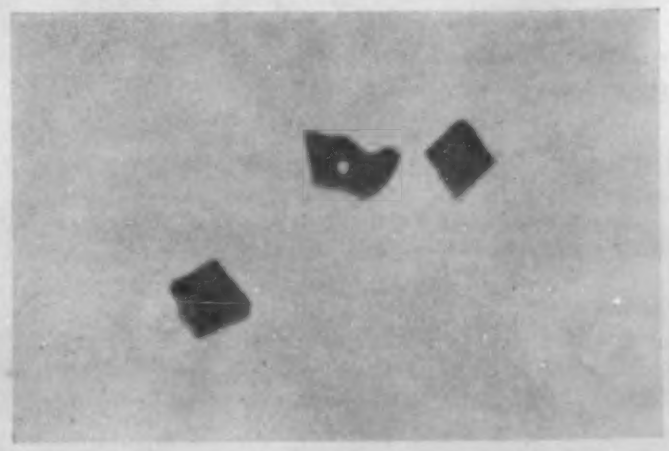
H. A. SCHWARTZ,
Mgr. of Research.

National Malleable and
Steel Castings Co., Cleveland.

Crystalline Manganese Sulphide in Cast Iron

To the Editor:

In connection with Mr. Ellis' discussion ("Crystalline Manganese Sulphide in Chilled Cast Iron" by O. W. Ellis, METALS AND ALLOYS, August, 1937, p. 221) of crystalline sulphides he found in cast iron, I would like to submit a photomicrograph of crystalline sulphides found in a medium manganese-chromium steel. Such sulphides are quite characteristic of this type of steel, especially when the steel is well oxidized.



C. E. SIMS.

Battelle Memorial Institute, Columbus, Ohio.